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A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, D.Sc., F.R.S., &c.

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THE CHEMICAL NEWS.

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No. 2458.—JANUARY 4, 1907.

NIOBIUM, TANTALUM, AND TITANIUM: OBSERVATIONS ON.

By W. B. GILES, F.I.C.

THE study of these metals has acquired additional interest through the remarkable researches of W. Bolton and M. Feuerlein, of the firm of Messrs. Siemens and Halske, who have achieved a veritable chemical and metallurgical triumph in transforming tantalum from the state of powders of doubtful composition and purity into metallic ingots, sheets,* and wire of great tenuity, and endowed with very remarkable properties, such as excessive hardness and great resistance to chemical agents; according to these gentlemen, tantalum in its chemical properties approaches the noble elements. It can hardly be doubted that tantalum before long will be obtainable in the shape of weights, crucibles, basins, and other utensils for laboratory use, and that in such forms it will prove to be of great value. It may be objected that owing to its rare occurrence its price must always remain very high, but experience shows that demand soon created a supply in the case of thorium, and already tantalite and columbite are available to the extent of many tons. From accounts which have reached the writer, large quantities of tantalite exist in the northern territory districts of South and West Australia.† It seems probable that the success of the tantalum lamp will enable this enterprising firm to recoup itself for the very considerable expenditure that these researches, extending over several years, must have entailed before any return was possible; in any case, great credit is due to these gentlemen for the very able manner in which they have brought the difficult subject of the metallurgy of tantalum to its present satisfactory condition.

From the date of the discovery of columbium and tantalum in 1801 by Hatchett and Ekeberg, a kind of romantic interest has been associated with these bodies, and probably more controversies and differences of opinion about their nature have arisen than with any other group of metals. It will suffice to recall that Wollaston in 1809 proclaimed the identity of columbium and tantalum. In 1846 H. Rose claimed that there existed three metals, viz., niobium, tantalum, and pelopium, and that after this Kobell contended for the existence of dianium, Hermann for ilmenium and neptunium, and Nordenskjöld for euxenium. So the matter remained in a state of uncertainty till the researches of Marignac, who sought to demonstrate that all the observed facts could be traced to the presence of three metals only, viz., tantalum, niobium, and titanium. Marignac's results have, as a rule, been received as a solution of the disputed points. Yet, in the opinion of some able chemists, it is doubtful whether his experiments were altogether conclusive. In 1880, Prof. Mendeleeff said (CHEMICAL NEWS, xli., p. 83):—"In my opinion it is in those numerous but insufficiently studied minerals, minerals with complex compositions, and containing titanium, zirconium, and niobium, that we should look for ekasilicon, *as well as for several other unknown elements*." The great resemblance between the properties of ekasilicon and titanium allows us to suppose that ekasilicon has escaped observation, although it was present in titaniferous minerals; the difference of the results relative to the equivalent of titanium leads to this supposition. To determine the atomic weight of titanium, Rose (*Pogg. Ann.*, xv., p. 145), Pierre (*Ann. Chim. Phys.*, xx., p. 257), and Demoly (*Ann. Chim. Phys.*, xxii., p. 213) decomposed $TiCl_4$ by water, and having weighed the Cl present they obtained the following results:—

Rose	From	48·08 to 48·48
Pierre	„	50·34 „ 49·55
Demoly ..	„	57·3 „ 55·90

It is difficult to attribute such a want of concordance to differences and errors in the processes of research of the different investigators; we should rather admit that the $TiCl_4$ contained foreign unsuspected matter.* . . . "I would mention that on several occasions new elements have been supposed to have been discovered in the compounds of titanium, niobium, and zirconium, and some researches lead us to think that ekasilicon might have been present in some cases. We know that Hermann believed that he had discovered ilmenium, although Marignac (*Archives des Sciences Naturelles*, January, 1866, and August, 1867) showed later on that the columbites, which had been suspected of containing ilmenic acid, in reality only contained a mixture of titanic, niobic, and tantalic acids. To confirm Marignac's assertion, which was that Hermann's ilmenic acid was only a mixture of titanic and niobic acids, we can say that the equivalent of ilmenium found by Hermann occupies the place between the equivalents of—

$$\mathrm{Ti}\left(12\frac{48}{4}\right) \text{ and of } \mathrm{Nb}\left(19=\frac{94}{5}\right).$$

* The author is indebted to the courtesy of Messrs. Siemens and Halske for the gift of two pieces of pure sheet tantalum. In hardness and general appearance it closely resembles iridium, except that the tantalum is not quite as white in colour.

† *Opening up an Australian Goldfield.*—Developments of the Pilbarra Goldfields in the northern territory of Western Australia are at present in their infancy, and, considering the isolation of the fields, this is not altogether surprising. Tantalum-bearing ores have been worked, and up to the end of 1905 71 tons, valued at £8925, have been raised.—*Times Financial Supplement*, Dec. 24, 1896.

* Kokscharoff has described under the name ilmeno-rutile a body analogous to rutile but which has the density =4·8, whilst ordinary rutile has the density 4·2.

But Marignac himself has not succeeded in finding an exact method for the separation of titanic from niobic acid; he himself admits that his process (based upon the difference of solubility of the double fluorides of potassium) is insufficiently complete. We have therefore a perfect right to be sceptical of the exactness of his results, however reasonable they may seem, and I further hold that a repetition of his work would not be superfluous, more especially as Ti and Nb can be separated in the form of chlorides, compounds whose boiling-points show considerable differences." In 1886, Mendeleeff's brilliant prediction of the existence of ekasilicon was verified by the discovery of germanium by Clemens Winckler, and a little later on his surmise that this body would be discovered in certain minerals containing tantalum, niobium, and titanium was also verified (Krüss and Nilson, *Ber.*, 1887, xx., 1696). Prof Moissan in his "Traité de Chimie Minerale," vol. ii., p. 561, says:—"Germanium is one of the rarest of the elements; however it seems to be diffused in many of the minerals containing niobium and tantalum. The absence of sufficiently delicate analytical reactions is unquestionably a predominating cause for the want of success in the search for this element in minerals which may contain it in small quantities. Germanium has been found in euxenite (Kroutschoff, *Journ. Soc. Chem. Russ.*, 1892, 130), samarskite, niobite, tantalite, and gadolinite." In 1887, Krüss and Nilson (*Œfvers af k. Swenska Akad.*, 1887) investigated the acids contained in fergusonite on the lines indicated by Marignac. Their results showed that by following this chemist's instructions they were unable to obtain any fractions which agreed with the formula of a pure niobium potassium oxyfluoride, the first obtained crystals showing an atomic weight for the acids superior to niobium, and in which they could not detect tantalum, while the last obtained crystals showed in the acids a much lower atomic weight than that of niobium; the cause of this was found in great measure to be due to the presence of titanium. They point out that when titanium and niobium occur together their double fluorides with potassium possess quite different solubilities in water to what they possess when taken singly, and that a separation of the bodies by this method is hopeless. They suggest that there are three acids present, one having a higher atomic weight than niobic acid, *which is yet not tantalic acid*, and one lower which they found to be titanic acid. It is possible that the body with the atomic weight higher than niobium may be one of the still missing bodies pointed out by Mendeleeff; this would have an atomic weight of about 100, and would just fill the gap pointed out in his tables of periodicity above molybdenum. In this connection it may be mentioned that the author in working upon yttrotantalites and Australian tantalites has obtained on more than one occasion acids, both hydrated and anhydrous, of a very decided blue colour; when these acids were ignited the blue colour became somewhat duller. In these blue oxides no tin or tungsten could be detected; *they were not products of reduction*; for heating with concentrated nitric acid did not alter the colour, nor did very long continued heating over a powerful blast-lamp have any effect in oxidising them to colourless bodies.

The further investigation of these three metals has been undertaken with much energy and perseverance by American chemists, and notably by Dr. Edgar F. Smith, R. D. Hall, C. W. Balke, M. H. Bedford, C. H. Warren, M. E, Pennington, T. B. Osborne, and Dr. A. A. Noyes, and yet, notwithstanding the undeniable advance that their researches have achieved, it is admitted that much remains to be done before the problem of satisfactorily separating these bodies can be said to be solved. In fact, Dr. Noyes says (CHEMICAL NEWS, xciii., p. 180):—"The quantitative separation in the wet way of the three elements, titanium, niobium, and tantalum, is also, we believe, still an unsolved problem. . . . It then remained to devise a plan for the detection of titanium and niobium. No satisfactory method of separation could be found." Mr. C. H. Warren says (CHEMICAL NEWS, xciv., p. 298):—"There appears to be, so far as the writer can discover, no method by which more than a rough approximation towards a quantitative separation of these elements can be effected." So by a consensus of opinion it is admitted that the accurate separation of these three bodies when they exist together is one of the most difficult problems in analytical chemistry. Separately they may be estimated with considerable accuracy, but when they are associated they exhibit such properties that they may be said to have lost their individuality.

The author having studied the literature of these metals, as far as they were accessible to him from the time of H. Rose forwards, has been led from time to time to test the accuracy of the methods that have been proposed for their detection, being induced to do this from observing that some of the statements made are inaccurate and some are contradictory. In a very recent work (Moissan, "Chimie Minérale," ii., p. 130), niobic acid is said, for instance, not to be reduced in a hydrochloric acid solution when alkaline fluorides are present, while in the same work, two pages further on, this very reduction is given for its estimation! Some of the methods proposed for the opening up of these rather refractory minerals have been studied, and also the best means for obtaining the three metals in the form of pure compounds. It is hoped that some account of what has been observed may be of interest to those who are workers in the same field. In the analysis of minerals containing these acids we obtain usually a white heavy precipitate which may contain all or any of them. It is very desirable to be able to ascertain quickly the nature of this precipitate, and to obtain, at any rate, a rough idea of the relative proportions of its constituents. It is well, also, to keep in mind the bodies that may occur in such minerals. We may encounter, for instance, tin, tungsten, antimony (not at all uncommon in Australian tantalites), lead, germanium, zirconium, tantalum, niobium, titanium, uranium, thorium, cerium, and the rare earth metals generally, besides the ordinary matters, such as silicon, iron, aluminium, &c. It is a curious fact that if we consult ths latest edition of Dana's "Mineralogy," where the analyses of over fifty analyses of columbites and tantalites are given, many of these being of recent date, that in only one instance is the presence of titanic acid recorded, whereas the experience of Marignac, Dr. Edgar Smith, and others show that it is a common constituent of these minerals, and that in some of them at least it occurs in rather considerable quantity. This also agrees with the experience of manufacturers who, since the developments of Messrs. Siemens, Halske, and Co., have worked up considerable quantities of tantalites and columbites.

Assuming, however, for the sake of clearness that we have obtained the heavy white precipitate from the fusion of the mineral with an alkaline bisulphate or in any other convenient manner, and that we are only concerned with the detection therein of tantalic, niobic, and titanic acids, we proceed to test it in order to distinguish the three bodies. Putting aside the methods described by Levy and others, which employ various alkaloids, pyrogallic acid, &c., in conjunction with strong sulphuric acid, as they have been shown by Dr. Edgar Smith to be unreliable, we are compelled to rely upon the fact that these three acids exhibit different reactions when treated with reducing agents. It seems to be generally conceded that tantalic acid cannot be reduced in the wet way to any lower form of oxidation. Niobic acid under similar circumstances is reduced to blue or brown compounds, while titanic acid also yields violet or brown bodies. However, if such tests are made in the ordinary way described in the text-books, difficulties are at once encountered, If the three acids are fused with alkali, treated with hydrochloric acid, and then with zinc as is generally indicated, we do not obtain any decisive result unless the niobic or titanic acids are present in relatively large amounts to the tantalic acid, and even if tantalic acid is absent it is often difficult to distinguish between the colours yielded by niobic and

titanic acid. This experience will no doubt be familiar to those who have tried the test. Prof. Joly ("Encyclopedie Chimique," iii., p. 13) says, when speaking of this reduction :—"Cette coloration ne se produit pas avec un acide niobique tantalifère." The reasons why this process is unsatisfactory seem to be evident and to be three in number :—

1. The acids are for the most part precipitated *in an insoluble form*.
2. In this *insoluble form* the acids appear to have the property of combining with the reduced oxides as fast as they are produced, forming possibly, for instance, such substances as niobous-tantalate (?), $Nb_2O_3Ta_2O_5$. If we take, for instance, niobic acid and add a large amount of tantalic acid, and test it as above described, we realise Prof. Joly's experience, and instead of a blue solution obtain merely a slate-coloured precipitate.
3. The fact that the acids are for the most part in an insoluble form makes the reduction with rod or granulated zinc a very slow process, and thus gives every facility for the formation of the insoluble compounds alluded to in No. 2 as well as for the absorption of oxygen from the air.

It is thus evident that to make this test a really practical one we must—

First.—Effect the reduction as quickly as possible.
Second.—Obtain *all* the acids in a soluble form.
Third.—Modify the test in some way so that niobium and titanium may clearly be distinguished.

When these conditions are realised the tests become very delicate and satisfactory. Moreover, the saving of time effected is very great ; decisive results are obtained in a few minutes which cannot be obtained in hours (if at all) when the old methods are employed.

(To be continued).

CHINESE TIN.

By FRANK BROWNE, Government Analyst, Hongkong.

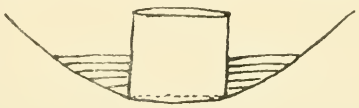
From Chinese information it has been ascertained that from 4000 to 6000 tons of tin arrive annually at Hongkong from the mines of Yunnan. The greater part of this is received during May, June, and July, when the West River is high enough for the carriage of the metal. The tin as imported is usually in flat rectangular plates, 1 in. thick, 2 ft. long, and 1 ft. wide. There are three qualities, of which the first and second are sometimes equal to those given below, but the third contains sometimes more than 20 per cent of lead. Most of the tin after importation is refined at the native refineries, of which several have been set up here in recent years. The arrival of tin from Chinese mines was first noticed in Hongkong in 1902. Three qualities are exported from Hongkong, and the following table shows their composition :—

	No. 1.	No. 2.	No. 3.
Tin	99·5—99·8	98·6—99·3	95·0
Lead	0·1—0·4	0·1—0·7	4·0
Antimony	0—0·1	0·02—0·3	0·02—0·3
Price per picul of 133⅓ lbs. in 1906 (dols.)	98—99	95—96	93—94

It is stated that about 70 per cent of the tin exported is of No. 2 quality. A good deal of the metal goes to Shanghai and other northern Chinese ports ; the balance is exported to Germany, England, and the United States.

Chinese Refining Process.

The plant for refining consists of a round iron pan, concave, 3 ft. across by 1 ft. deep, having in its centre, but not attached to it, an iron cylinder open at both ends, 1 ft. high and 1 ft. in diameter. Two of these pans, imbedded in brick-work, are placed side by side. They are heated from below by means of billets of wood. A filter layer 5 in. thick composed of the dross from former tin meltings, is attached to the cylinder in the first pan. The cylinder in the second pan has no filter, as this pan is used only for the separation of tin from dross, for which operation a filter is unnecessary. Tin is put into the first pan, and the molten metal is allowed to filter into the cylinder. A quantity of purified metal soon collects. This is "tossed" and skimmed, and the skimmed liquid is then ladled into moulds. The ladle holds about three pints of liquid, and each ladleful in the mould is at once skimmed ; about three ladlefuls are sufficient to fill one mould. The skimmings of the metal in the first pan and cylinder are put into the second pan, and a further quantity of purified



Chinese Tin Refining Pan,
Showing filter of dross attached to the cylinder.

tin is collected in its cylinder. From time to time when no more tin runs, the semi-solid dross in the first pan (except the filter dross attached to the cylinder) is transferred to the other pan, and more tin is put into the first pan to be melted as before. During the refining a small ingot is cast, and from its general appearance the quality of the tin is judged. The dross is finally cut out from the second pan into slabs of about 10 lbs. weight. These slabs are heated with charcoal in a wind furnace, and the resulting metal allowed to run off into a hole. From this hole it is transferred to the melting pans to be purified. The residue from the second or charcoal purification is a dark brown porous solid, inclined in parts to fall to powder. It consists mostly of metallic iron, with some tin, lead, silica, sulphur, and charcoal, and small quantities of arsenium and antimony. No tungsten, bismuth, copper, silver, or gold is present. This is sold to buyers at Shanghai at 10 dols. a picul, where it is said more tin is extracted, and the residue therefrom made into iron articles.

Analysis of Chinese Tin.

Five grms. of drillings are treated in a flask with 50 cc. of nitric acid (about 1·3 sp. gr.), and when all action has ceased, the flask contents are transferred to a basin, and evaporated over a water-bath to complete dryness. The residue is boiled several times with water to dissolve out lead, until the filtered washings do not darken with ammonium sulphide. The residue is then boiled with a 5 per cent solution in water of pure tartaric acid to dissolve out any antimony, and the residue, after transferring to a filter, is washed three or four times with boiling water. The tin residue is then dried, gently incinerated, allowed to cool, and 1 cc. of nitric acid is poured over it. After very gently heating for a few minutes, the crucible is blasted in the usual manner, and the tin weighed as oxide. The lead in the washings is estimated either as sulphate, or when the quantity is small, the washings may be treated with a drop of ammonia, then acidified with acetic acid, and the lead estimated colorimetrically by sulphuretted hydrogen. It must not be forgotten, however, that arsenic acid, iron, and zinc may occur with the lead in the washings. The tartaric acid washings are nearly neutralised with ammonia,

and the antimony is then best estimated by comparison with an antimony solution containing 1 mgrm. of antimony in 1 cc. of 5 per cent tartaric acid solution, both of which are heated and treated with sulphuretted hydrogen. The amount of antimony sulphide is usually under 10 mgrms., and this method for minute quantities of this metal has been found more satisfactory than gravimetric methods.

The above is not a new process, but the method of procedure therein specified has been found very useful for Chinese tin. A little care is required in washing the tin oxide, but the filtrate after returning once to the filter usually comes through quite bright. Care should be taken with the washings containing the lead, so that they may if necessary be searched for any loss revealed by the analysis. If the first gentle incineration of the tin oxides be omitted before adding the nitric acid, the oxide after blasting may not be of a uniform colour. This darkening in parts is due to the action of a trace of tartaric acid remaining in the oxide.

SOME SOURCES OF IMPURITIES IN C. P. CHEMICALS.*

By J. W. SCHADE.

THE elimination of impurities in chemically pure chemicals has long been the desire of chemists; but owing to a seeming indifference on their part, the manufacturers have not exerted themselves to make their products better than they deemed absolutely necessary to meet the demands. During the past year or two much increased interest has been manifested in the movement to secure the best grade of laboratory reagents consistent with economy in manufacture. To ask for a reagent "absolutely pure" is to ask, in most cases, for the impossible in economical manufacture. The object of this paper is to present some sources of impurities in chemical reagents and to point out that there are limits of purity obtainable by manufacturers.

With few exceptions all reagents are shipped in glass containers. The dry salts probably do not take up impurities from the bottles, but acids and ammonia after standing in containers for a few days are contaminated with impurities from the glass. These impurities may be one or more of the following:—Iron, potassium, sodium, silica, calcium, and from bottles of Jena or "Nonsol" glass, zinc. In the case of ammonia, silica is the principal impurity from the glass; in the case of acids, iron. The latter is due mainly to the fact that small chips of iron oxide flake from the blowpipes used by the glassblowers, and although acid is allowed to stand in the bottles before they are washed for use, there are undoubtedly minute particles that escape immediate solution. Acids shipped in carboys having glass covers secured by zinc rings are liable to contamination from the zinc, owing to the splashing of the acid into the neck of the carboy. Hydrofluoric acid shipped in lead carboys takes up that metal as an impurity. The nature of these impurities is such that the liability of contamination cannot be entirely removed, though it may be diminished by the use of more resistant glass and of glass-stoppered carboys.

The second source of impurities is in the chemical works. It is the vessels in which the chemicals are manufactured. These vessels—tanks, stills, condensers, crystallising dishes, and so on—are made or lined with lead, silver, copper, iron, aluminium, nickel, zinc, platinum, porcelain, earthenware, or glass. The impurities from this source are the metals of which the vessels are made, and from the non-metallic receptacles silica, sodium, potassium, calcium, and iron. Iron vessels give rise to other impurities than iron, notably manganese. In the manufacture of sodium bismuthate, for instance, iron vessels cannot be used, owing to the contamination of the product with manganese, which, of course, is inadmissible in that reagent. Nickel is found in the best grades of caustic alkalis from the dishes in which they are made. Copper, aluminium, or silica are found in acetic acid from the condensers used in the distillation. Lead tanks are very generally used, especially for crystallising organic acids such as tartaric and citric. The author has also found it in hydrofluoric acid, ammonium chloride, potassium sulphate, and sodium chloride. The amount of impurities of this class is minimised by the judicious selection of vessels to meet the needs of each case. As with the first class, however, the liability to contamination cannot be entirely removed.

There is another class of impurities introduced during the purification of the salts. These impurities are reagents used to precipitate certain foreign substances or the salts formed by the reaction. For instance, the author once analysed a sample of sodium chloride in which sulphate had been precipitated by means of barium chloride. This salt gave decided tests for both barium and sulphate, an anomalous condition often met in testing reagents. Another example of this is the presence of calcium in ammonium oxalate. Samples of ammonium oxalate giving clear solutions sometimes contain some hundredths of a per cent of calcium though the solution from which the crystals were obtained was alkaline. It is evident from these facts that the so-called "insoluble precipitates" are dissolved to an appreciable extent by the concentrated solutions from which the salts are crystallised.

The final class of impurities includes those occurring in the original source of the chemicals. *i.e.*, in the minerals, and in those substances used in manufacture. These impurities will vary in number and kind, depending on whether the treatment of the mineral is simple or complicated. Sometimes it is impossible for the manufacturer to get rid of certain impurities without putting a prohibitive price on an article. Iron, alumina, and silica appear in all but the highest-priced grades of caustic alkalis and alkali carbonates. Nickel and cobalt cannot be entirely separated on the large scale cheaply. As has been pointed out above, calcium cannot be entirely removed from ammonium oxalate, strange as it may seem, without considerable trouble and expense. Again, strontium sulphate will not precipitate barium from a solution of strontium chloride or nitrate unless a large excess is added, in which case sulphate is introduced as an impurity. Here the manufacturer is compelled to choose the lesser of two evils. This is the inevitable alternative in many instances.

Calcium persists in barium salts, and if considerable calcium is present in the mineral from which the barium is obtained it is no easy matter to remove it. The removal of iron from copper sulphate is not as simple as one would imagine. Some of the "iron-free" copper sulphate sold on the market contains several thousandths of a per cent of iron. To separate the two iron must be in the ferric condition. Hydrogen peroxide is theoretically an ideal oxidising agent in that it introduces no impurity into the copper sulphate, but in practice nitric acid works somewhat better. Here is a case in which nitric acid is introduced as an impurity in preference to iron. Lead is sometimes found in copper salts and is difficult to remove from the chloride and nitrate. Ferric salts always contain free acid, fused magnesium chloride always contain ammonia, and caustic alkalis and alkali carbonates, as has been said, almost always contain iron, alumina, and silica.

These illustrations serve to show that at ordinary prices chemical reagents must be limited in purity. This, however, is not a serious difficulty except in cases when extraordinarily accurate work is to be performed; and the manufacturer can supply at a reasonable price reagents that will give accurate results when put to the ordinary uses. —*Journal of the American Chemical Society*, xxviii., No. 10.

* Read at the Ithaca Meeting of the American Chemical Society.

ON A NATURAL SYSTEM OF ARRANGING THE CHEMICAL ELEMENTS, IN WHICH THEY FALL INTO THE PERIODIC GROUPS, BASED SOLELY UPON THE ATOMIC VOLUMES AND THE COMBINING WEIGHTS.

By the late JAMES MONCKMAN, D.Sc.

One of the most interesting things in the whole course of chemistry is the law that the properties of the elements bear a periodic relation to their combining weights. But when this law is used for the classification of the elements there are some things that seriously detract from the satisfaction with which it is regarded; firstly, it does not give a fixed order for the groups; secondly, there is a certain irregularity, there being no representatives of the heavier elements in the first two lines; and, thirdly, the triplets Fe Co Ni, Ru Rh Pd, Os Ir Pt, are left out in the cold in an eighth column all to themselves. These have led to so much confusion that it is easy to read half-a-dozen different arrangements of the elements in as many different books on the subject.

Gold and platinum trouble some writers, while others take sodium out of the alkaline metals and place it at the head of the copper group, in order that these two may be of equal length, repeating the process with magnesium, &c., so getting an artificial regularity, but at the same time spoiling the natural order of the members of each group. Whereas, authors wishing to give special importance to some particular group simply transpose the whole so that the group in which they are interested may be first in order, or may occupy the centre, while they explain it by saying this is one of the ways in which the groups may be placed.

Now while variety is pleasing in art and decoration, it cannot by any means be considered so here, and therefore a method at once simple and effective, that will get rid of this confusion, should be welcomed, more particularly if it gives us reason for placing such bodiss as the triplets in a position of prominence proportional to their importance, and also arranges the other groups in situations relative to these, or to a fixed central line, such as their properties appear to indicate.

The first hint of the possibility of any such plan was given by a diagram showing the relation of the combining weights of the elements to the heat produced when they combined with chlorine, which was published by Laurie in the *Phil. Mag.*, [5], xv., 42. This was produced by marking off the combining weights of the elements upon the horizontal line in checked paper and the heat of combination upon the vertical line. In this way he got a series of points, which, being joined by lines in the order of their combining weights, gave the diagram required. Now instead of following Laurie's method of joining by lines in order of the combining weights, connect the elements of the same periodic groups, and seven lines are produced by joining Li, Be, B, C, N, O, F, or Cl to the other members of their own groups; and although these are somewhat wavy, they have a general kind of parallelism which at first impresses one with the idea that something new and important has turned up; but when the heavier metals are joined into groups, the lines, although parallel to each other, are not so to the previous groups, but cut across them in a confusing manner, completely dissipating any feeling of jubilation that the regularity of the first set produced. Here were two distinct sets of lines, the lighter metals and the heavier, but nothing more could be done to find out why they were similar and why they differed. They did a good thing, however, by rousing the attention to the possibility of the existence of an underlying system, but my search for it was without avail, until I read Prof. Lothar Meyer's account of the Atomic Volumes and their Relation to the Combining Weights and to the Periodic Law, when the full signification of the matter became apparent.

In his "Outlines of Theoretical Chemistry," Meyer gives a table of the elements arranged according to the periodic law, includes in it the densities of the elements, and the atomic volumes, which is of course calculated by dividing the combining weights by the density in each case, and he shows that the volume falls as the atomic weight rises to a certain point, after which they increase together. This he has also shown in a graph in which the combining weights are taken along the horizontal line and the atomic volumes upon the vertical one (Fig. 1).

The first curve is formed by joining Li, Be, B, C, N, O, and F together, and its lowest point is at c. The second line joining Na, Mg, Al, Si, P, S, and Cl, forms the second curve, but the whole is higher above the zero line. The third curve is larger, and the lower elements form a kind of basin-shaped depression in the lower part; the same occurs in the fourth. The fifth and sixth are imperfect.

The very great importance of the relationship expressed by this graph has apparently, escaped the notice of chemists, nor has the fact been perceived, that by a very slight alteration of the method of constructing the graph, the elements fell into such positions that the lines joining those of the same periodic groups form a series of concentric curves, thus deducing the periodic arrangement from the combining weights and the atomic volumes alone, and in addition producing a system symmetrical about a zero line.

Prof. Meyer drew attention to the fact that, "Where each curve changes direction from descending to ascending many important properties of the elements change also. Thus in the front part of the curve, where the volumes decrease as the combining weights increase, the elements are paramagnetic, malleable, and usually form stable compounds with oxygen, while in the other half or ascending portion the elements are diamagnetic, brittle, and the oxides are easily reduced."

It is therefore quite clear that the change in the curve indicates a change in some important characteristic of the elements in relation to the combining weights.

The curve is similar to that which is formed when a thermocouple is heated with gradually increasing temperature until the neutral point is crossed; thus if we take rods of copper and iron and form a couple, and, while keeping one end at 250° C. we vary the temperature of the other, and plot the quantity of electricity produced, a similar curve is formed descending to zero and then ascending with a changed sign. Now we know that the electrical state of each metal in this case can be represented by a straight line, and the action of the two together by two lines crossing at the zero point.

In like manner the atomic volume and the combining weights may be represented by lines crossing each other at the zero or turning point of the curve. By this means Fig. 2 may be produced. There is, however, another way of getting the same diagram which is more logical, and this consists in taking the combining weights as before, but plotting the tangents of the angles that Meyer's curves form with the horizontal line instead of the volumes. This causes the rising curve to be thrown upon the opposite side of the zero line, and when the elements of the same periodic groups are joined by lines, ten concentric curves are formed, each having the appearance of being part of an elliptical figure, with one side considerably flattened.

To get the elements in this diagram to arrange themselves in the order usually adopted in books, and the natural one for people writing from left to right, it is necessary merely to change the usual convention as to the signs and making the positive take the left side, and the negative the right, while the combining weights are measured upon the vertical or zero line. By this means Fig. 2 is constructed. (For explanation of Fig. 2 see p. 6).

These curves arrange themselves naturally into three sets, to which, for convenience of reference, the name Exionic, Endionic, and Central have been given.

The exionic lines are numbered 1 to 4 and constitute the four curves that cut the transverse lines AB and CD. Upon them are situated the lightest elements.

TABLE I.

First.—Both sides of the zero line are alike quantitatively.

ZERO LINE.

Left or + Side.	*Right or − Side.*
1. The atomic volumes decrease as they approach the zero line (Fig. 2).	The same takes place on this side.
2. Chemical affinity also decreases.	1, 2, and 3 fall, while 4 and 5 rise.
3. Power of producing heat when they combine with another element does the same thing.	
4. Melting points, and	
5. Atomicity rise.	

Second.—They differ qualitatively on the two sides.

ZERO.

1. Prof. Meyer gives the first four. As the atomic volumes decrease the combining weights increase.	As the atomic volumes increase the combining weights do the same.
2. The elements are paramagnetic (attracted by a magnet).	The elements are diamagnetic (repelled by a magnet).
3. They are malleable.	They are brittle.
4. Their oxides are stable.	Their oxides are easily reduced.
5. All the exionic elements are metallic except one.	All the exionic elements are non-metallic or semi-metallic except one.
6. They are electrically positive to those on the opposite side.	These are negative to those on the opposite side.
7. The affinity for oxygen is greater further from the zero line.	The affinity for hydrogen is greater further from the zero line.
8. Exionic oxides nearly always bases.	Exionic oxides mostly acids.

Third.—Their variations are symmetrical.

ABOUT THE ZERO LINE.

1. With the exception of the first two lines, they become gradually more distinctly metallic as they approach the centre.	The same thing takes place on this side also.
2. If the volumes of unit weights of the elements be plotted upon checked paper, with the combining weights measured in one direction and the volumes at right-angles, the diagram shows a series of concentric curves shaped like the outline of one-half of a Florence oil flask—that is, spherical in front, but tapering off behind.	The curves formed by the elements on this side complete the figures of the Florence flask. The whole forming a set of ten more or less perfect figures, symmetrical about the zero line and decreasing gradually in size. Somewhat similar to Fig. 2, but very much wider at C D and E F, and much closer at I J and K L.

3. Atomicity.

Exionic curves	.. ..	No. 1 are monads on both sides.
„	.. ..	No. 2 „ diads.
„	.. ..	No. 3 „ triads.
„	.. ..	No. 4 „ tetrads.
Endionic	.. ..	No. 5 „ triads.
„	.. .. ..	No. 6 „ diads.
„	.. .. ..	No. 7 „ diads. (On the negative side it is irregular, being both 1, 2, and 3).
Central	.. .. ..	All are diads.

4. Spectroscopic lines. Meyer's law (*Nature*, August 24, 1899, p. 394). If the wave-lengths for all the lines for N – be calculated and put as ordinates and the atomic weights as abscissæ, then all the points lie on a curve similar to that which gives the atomic volumes.

TABLE II.

Set ... ... / Rise or fall ...	Exionic Gradual		Endionic Gradual		Central Gradual		Endionic Gradual		Exionic Gradual	
	From	To	From	To	From	To	From	To	From	To
5. Density	1·1	4	7·5	11	14·1	13·9	13	8·3	7·9	2·7
6. Melting-point	350	1700	1500	1600	2200	1770	1300	760	480	240
7. Refractive equivalent .	9·3	14·6	24 (Single elements).	11·7	17	16	16	20	20	9
8. Specific heat of unit vol.	0·3	0·76	0·6	0·9	0·7	0·8	0·7	0·4	0·57	0·25
9. Atomic heat	6·7	5·9	7·4	6·7	6·3	6·3	6·1	6·2	5·9	6·1

EXPLANATION OF FIG. 2.

The dots represent the positions of the elements. The names of these upon each transverse line are as follows :—

Upon (A B)	Li	Be	B	C													C	N	O	F
„ (C D)	Na	Mg	Al	Si													Si	P	S	Cl
„ (E F)	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni				Cu	Zn	Ga	Ge	As	Se	Br
„ (G H)	Rb	Sr	V	Zr	Nb	Mo					Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
„ (I J)	Cs	Ba	La	Ce	Di															
„ (K L)					Ta	W					Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
„ (M N)				Th		U														
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	10.	9.	8.	7.	6.	5.	4.	3.	2.	1.

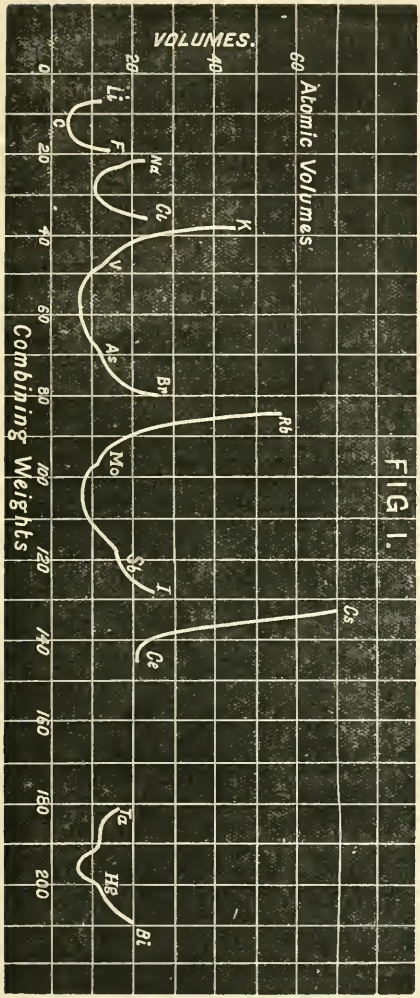

VOLUMES.
Atomic Volumes.
Combining Weights
0
20
40
60
80
100
120
140
160
180
200
Li
C
F
Na
Cl
K
V
As
Br
Rb
Mo
Sb
I
Cs
Ce
Ta
Hg
Bi

FIG. 1.

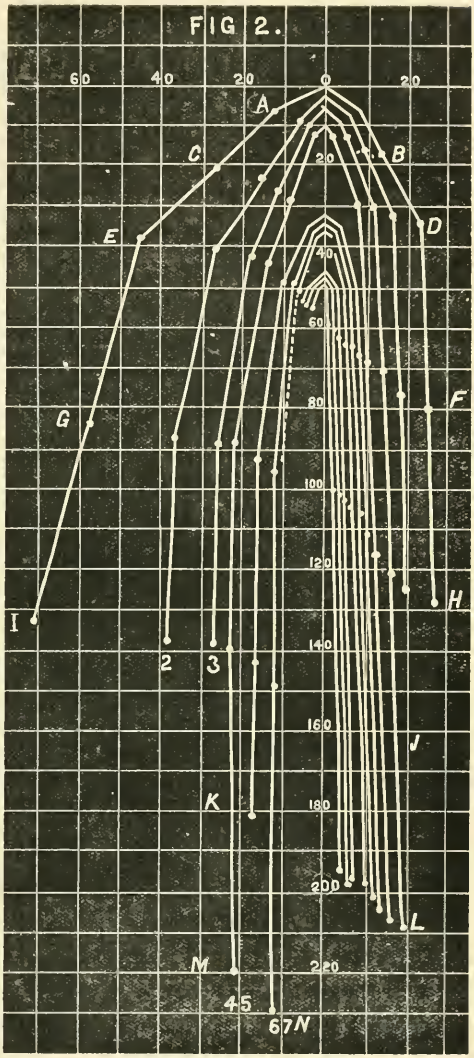


FIG 2.
60
40
20
0
20
A
B
C
D
E
F
G
H
I
J
K
L
M
N
2
3
4
5
6
7
40
60
80
100
120
140
160
180
200
220

The endionic numbered 5. 6, 7, are the three next within these, and they have the heavier elements; these curves do not cut AB.

The central consist of three lines near the centre containing the heaviest elements in each transverse line, and their natures are so closely allied that they are always put into one column; they form triplets Fe, Co, Ni on EF, Ru, Rh, Pd upon GH, and Os, Ir, Pt upon KL. The centrals are remarkable metals, at one end the most magnetic and at the other the densest and the most intractable. Outside the whole will be the curve upon which He and the other monads fall, occupying places beyond F, Cl, Br, and I, while H is upon the other side, alone, but spaces are left vacant for other elements with combining weights of about 5, 21, and 38.

This Natural System of Classification, while losing nothing that is good in the plans usually adopted with the periodic groups, has a great many advantages; in addition to fixing the positions of the lines it has three qualities that must be found in any perfect system of classification.

1. Bodies on opposite sides of the zero line should differ from each other in certain important qualities, and
2. Where their properties are capable of being expressed quantitatively they differ in the ratio of their distances from the zero line, or nearly so.
3. When sudden changes take place in passing from the Exionics to the Endionics and again to the Centrals they should, as a rule, repeat the process in the reverse order on continuing their way from the centre to the other side.

All these three are formed in the natural system, which is really the Periodic Law in its greatest simplicity applied to the classification of the elements.

This may be put into tabular form, as in Table I.

Consequently if these be treated in the same way as the atomic volumes in Fig. 2, a similar figure will be produced. with similar symmetry about the zero.

In order to get rid of irregularities produced by experimental errors, impurities, allotropic forms, or other chemical or physical changes, it is necessary to use averages of the members of each group and not to rely on single elements. In Table II. the averages of the first and the last group of each set are given and the way in which the averages of the intermediate members rise or fall is indicated by reading the head line for each. Thus, density in the exionic set, rise gradually from 1·1 to 4; atomic heat falls gradually from 6·7 to 5·9. The refraction equivalent (7) is taken from Gladstone's table in "Watts' Dictionary," iv., 227. In the case of the endionics V, Cr, Mn, only are given in the table, so that averages could not be taken, hence the rate of decrease is probably too violent. Generally, the change in the numbers is gradual in each set of groups, sudden in passing across the division line, frequently with change of direction afterwards, and the process is reversed on the other side.

In another paper I hope to show how these atomic volumes may be used to calculate the thermal equivalents by means of an equation involving the volumes of the elements before union, and of the salts after combination, together with a constant that varies from curve to curve in a fairly regular manner about the zero.

Although these are not all the lists that could be made, they are quite sufficient to show the extreme importance of the atomic volume and its great value as a means of obtaining a classification of the elements which is at once simple and inclusive.

Table III. is given in full to show how the figures in the foregoing list are obtained. It had, however, one additional characteristic that is worth noting: the horizontal averages for the exionic and for the endionic sets indicate some particular connection between the elements of the same line, which produce a constant average, and consequently whenever any single elements such as C and B have exceptionally high melting points, the other elements of the line have proportionally low ones to compensate.

The averages of all the lines of the exionics lie between 600 and 700, but in the first line C is 2000 and B 1300;

TABLE III.—BOILING-POINTS.

Melting-points in Absolute Temperature.—H, 32; He, ?; Ne, 32; Kr, 121 (*a*), 164 (*a*).

(*a*) Includes Ta, W, &c., as there are no elements in the proper line.

Li	455	Be	1173	B	1300 ?	C	2000 ?																	N	91	O	91	F	150
Na	369	Mg	873	Al	973	Si	1773																	P	317	S	387	Cl	168
K	336	Ca	973	Sc	—	Ti	2000 ?	V	1500	Cr	1500	Mn	1600	Fe	1800	Co	1793	Ni	1673	Cu	1327	Zn	700	Ga	300	As	773	Se	953	Br	266
Rb	312	Sr	973	Y	—	Zr	1773	Nb	1500	Mg	1500			Rh	2300	Ru	2010	Pd	1773	Ag	1473	Cd	590	In	480	Sn	506	Sb	696	Te	738	I	387
Cs	299	Ba	1008	La	1073	Ce	1073	Ta	1500	W	1500			Os	2700	Ir	2100	Pt	1900	Au	1528	Hg	238	Tl	577	Pb	600	Bi	541				
	1771		5000		3346		8629		4500		4500				6800		5903		5300		4128		1567		1327		2279		2418		2169		971
Av.	354		1000		1115		1726		1500		1500		1600		2233		1967		1770		1376		513		442		760		483		542		243

Horizontal Averages.

In outer exionic curves, or lighter elements—		In inner endionic curves, or heavier elements—		In central triplets—		For the whole line—		Differences.	Differences in combining weights.
Li line	660	V line	1150	Fe line	1773	Li	666	28	16
Na „	694	Nb „	1070	Ru „	2073	Na	694	36	16
K „	600					K	1039	50	46
Rb „	660			Os „	2300	Rb	1082	50	48
Cs „	700	Ta „	1070			Cs	1130		

these are counterbalanced by the very low melting points of N, O, and F.

Another point to be noted is similarity in the rise in the differences in the melting points and in the combining weights for the whole line.

The gradual rise of the numbers in the exionic with sudden fall on passing, then another gradual rise in the endionics with another sudden rise between them and the centrals where there is a gradual fall, the whole being repeated in the inverse order to the end, is well shown in the line of averages.

THE USE OF PORCELAIN DISHES IN SILICA DETERMINATIONS.

By F. L. KORTRIGHT.

In the usual method for the determination of silica, after the substance has been gotten into solution, it is evaporated to dryness to render the silica insoluble. For this evaporation most writers recommend the use of platinum dishes instead of porcelain dishes without stating their reasons for so doing, but the opinion seems to prevail that the objection to the porcelain dish is the possibility of a portion of the dish going into solution and by this means increasing the amount of the silica. The first to call attention to the other possibility, that the porcelain might cause a loss of silica, was W. F. Hillebrand, who says (*Journ. Am. Chem.* xxv., 1192) "Were it not for the fact that similar deficiencies do not appear in their cement analyses, it might be thought that in some of the cases silica had adhered so tenaciously to the porcelain dish on evaporation as to escape complete removal. This is a cause of error quite likely to arise at times when using porcelain, because of the difficulty of seeing the adhering silica against the white surface." Later H. N. Morse says ("Exercises in Quantitative Chemistry", 311), "It is very difficult to distinguish small particles of silica upon a concave surface of white porcelain, and almost impossible, therefore, to determine whether a dish of this kind has been sufficiently cleansed."* So far as I can find in the limited literature at my disposal, no data has been published, however, showing the possible extent of the error which may be introduced into a silica determination through being unable to remove all the silica from the dish, and Dr. Hillebrand has informed me that he has not made any quantitative determinations of the amount of silica which might be thus lost.

The impression gained from both of the statements quoted above was that the silica escaped determination on account of its not being seen on the white porcelain, and not because it adhered so tenaciously that it *could not* be removed. The following, however, has to do entirely with the silica that it was not possible to remove from the dish by any ordinary means :—

For several years it has been noted in this laboratory that when porcelain dishes were used for this evaporation, a greater or less roughening of the glaze of the dish occurred at about the line where the surface of the liquid came at the beginning of the evaporation. Until recently we have believed that this roughening was caused by the action of the solution on the glaze of the dish, although no attempt was made to find if this were true. The following experiments indicate, however, that the roughening is caused by a deposit of silica on the glaze and not by a destruction of the glaze by the action of the solution.

The Argillaceous Limestone, sent out about a year ago by the Committee on Uniformity in Technical Analysis, was used in this work. In the first part of the work the limestone was decomposed by first blasting a weighed portion, then dissolving as much as possible in hydrochloric acid, filtering, igniting the residue, fusing it with sodium carbonate, and adding the melt to the original solution. Later the weighed limestone was mixed at once with about a-half grm. of sodium carbonate and fused. The melt was then treated with water and finally acidified with hydrochloric acid. The method of decomposition apparently had no effect on the silica determination, and the second method is much more convenient.

The solution obtained as above was evaporated as dry as possible on the steam bath. The residue was moistened with 10 cc. of concentrated hydrochloric acid, 50 to 100 cc., (depending on the size of the dish) of water was added, and it was digested on the steam bath for ten minutes. The silica was then filtered off and washed thoroughly. The filtrate and wash water were evaporated and treated as above. The filtrate from the second evaporation was made alkaline with ammonium hydroxide and the precipitate filtered out. In the first two determinations this precipitate was ignited and then fused with acid potassium sulphate, dissolved in dilute sulphuric acid, evaporated to white fumes, diluted with water, and the silica separated by filtration. In the rest of the work the precipitate formed by the ammonium hydroxide was collected and washed on a filter, dissolved at once in dilute sulphuric acid, and the ash of the dried and burned filter added. The solution was then evaporated to white fumes, diluted with water, and the silica separated by filtration.

The silica from the two evaporations was placed in a platinum crucible, the carbon of the filter burned, and the silica was then ignited over the blast for ten minutes, cooled, and weighed. The silica from the ammonium hydroxide precipitate was treated in the same way, and the per cent of silica was calculated from the total.

A few determinations of the silica were made with platinum dishes in order to determine the per cent of silica in the limestone. The other evaporations were made in porcelain dishes varying from 9½ to 15 cm. in diameter, some of which were set as low as possible in the steam, others so that only a small part of the bottom of the dish was in direct contact with the steam. Some of the dishes were covered quite closely with Victor Meyer funnels, others were left entirely open. In some cases new dishes were used, and in others dishes were used which had been used several times before and then thoroughly cleansed. None of these conditions apparently affected the results.

In the report of the Committee on Uniformity in Technical Analysis (*Journ. Am. Chem. Soc.*, xxviii., 229), Dr. Hillebrand gives the per cent of silica in this limestone as 18·11 and Dr. Waters gives it as 18·18. Five determinations which I made gave 17·93, 18·10, 18·11, 18·05, 18·01, or an average of 18·04 per cent. (In the first of these determinations the bottom of the platinum dish was a little rough and this *might* have caused a slight loss).

In the first determination in porcelain there was a heavy rough deposit left as a ring part way up the side of the dish, which could not be removed by rubbing with a "policeman," and the per cent of silica was found to be 17·09. The dish was then filled above this roughness with water containing ammonium hydroxide and heated on the steam bath for some time. (All of the ammonium hydroxide used in this work was freshly distilled and tested for silica). The solution was then acidified with hydrochloric acid, evaporated to dryness, taken up in water and hydrochloric acid, and filtered, A second treatment of the same kind left the dish bright and smooth, and the silica thus separated amounted to 0·88 per cent of the limestone, so that the total silica then amounted to 17·97 per cent, in very good agreement with that found in platinum. In another case the per cent of silica was found to be 17·58 and 0·38 was separated from the dish by the ammonium hydroxide treatment. In the other determinations only a faint stain was noted on the dish and the treatment with ammonium hydroxide was omitted.

The following results in per cent of silica were obtained, using porcelain evaporators (17·09+0·88), 17·71,

* I cannot agree with Professor Morse in this, for if the dish is rinsed with hot water it dries almost at once, and then particles of silica are easily seen on the shiny porcelain surface.

17·87, 17·77 (17·58+0·38), 17·81, 17·88, 17·96, 18·04, 18·07, 18·01, 17·98.

These results show that silica is not obtained from the dish when porcelain evaporators are used, but that there is usually a slight loss of silica from a portion adhering to the dish, and that occasionally this loss may be so great as to seriously affect the accuracy of the determination even for technical purposes. This silica adheres so tenaciously to the dish that it cannot be removed by ordinary means, but can be removed by heating with ammonium hydroxide.

Up to the present I have not been able to discover the conditions which cause the adherence of the larger amounts of silica, but I am convinced that the two cases quoted here are not isolated instances, but that similar cases will be found frequently.

These results show that, although platinum dishes are always to be preferred for the evaporation in silica determinations, porcelain dishes may be used satisfactorily for technical analyses if the dry dish is carefully examined after each analysis and no more than a slight stain is noted on the glaze. If a dull or rough surface, usually as a ring part way up on the side of the dish, is found, it must be removed and its silica added to the other, or the determination must be repeated.—*Chemical Engineer*, v., No. 1,

THE DETECTION OF BARIUM, STRONTIUM, AND CALCIUM.

By STANLEY R. BENEDICT.

THE distinctive features of the following method for the detection of the alkaline earth metals may be briefly summarised as follows:—1. In contradistinction to most, if not all other, methods, it provides for the removal of barium without the use of chromate or dichromate, thus giving colourless solutions for the subsequent detection of strontium and calcium. 2. It entirely avoids the somewhat troublesome operation of filtering solutions containing the precipitated sulphates of calcium, barium, or strontium. 3. The method is very rapid, the manipulation simple, and the results positive. The precipitates dealt with filter perfectly clear without difficulty.

The reagents used are saturated potassium iodate solution, dilute hydrochloric acid, ammonium oxalate, and saturated ammonium sulphate solution.

As preliminary to an outline of the method, it may be well to mention the following facts, upon which it is based:—

Barium iodate, while somewhat soluble in water, is practically insoluble in an excess of potassium iodate solution of proper concentration, even in the presence of a certain amount of hydrochloric acid. Barium is therefore completely precipitated from its solutions by an excess of potassium iodate, in presence or absence of dilute hydrochloric acid, the filtrate yielding absolutely no turbidity with sulphate or chromate solutions.

Strontium iodate is more soluble in water than is the corresponding barium compound. Like the barium salt it is completely precipitated from neutral or slightly ammoniacal solutions upon addition of a considerable amount of iodate solution, the precipitation taking place somewhat more slowly than with the barium compound. Unlike the barium salt, however, strontium iodate is quite soluble in dilute hydrochloric acid, and strontium is therefore only incompletely, if at all, precipitated by an iodate from its solutions which have been acidified with dilute hydrochloric acid.

Calcium iodate is more soluble than either the barium or strontium compound, and is only incompletely, if at all, precipitated from neutral, acid, or ammoniacal solutions, upon addition of an excess of iodate solution.

The precipitated iodates of all these metals form bulky, granular precipitates which filter clear very rapidly.

An outline for the procedure for the identification of calcium, strontium, and barium follows.

A portion (2 to 3 cc.) of the solution to be tested is acidified with one-half its volume of 5N hydrochloric acid, and to the liquid thus obtained its own volume of a saturated solution of potassium iodate is added. If a precipitate forms *at once*, barium is present. If no precipitate forms, barium is absent. If a precipitate forms slowly, either barium is present in low concentration or strontium is present in considerable amount. In such a case the presence or absence of barium should be confirmed by the addition of a few drops of dichromate solution to the original solution. This confirmation is rarely necessary.

Having established the presence or absence of barium, the solution is agitated and allowed to stand for one-quarter to one-half a minute. The precipitate is filtered off, and to a portion of the filtrate (not the first portion through the filter) is added a little more than an equal volume of a saturated solution of ammonium sulphate. The solution is then heated to boiling. A white precipitate, permanent on boiling, consists of strontium sulphate, and indicates strontium.

To another portion of the original solution is added two volumes of a saturated potassium iodate solution, the mixture agitated, and allowed to stand one-half to one minute, and filtered. To the filtrate is added some ammonium oxalate solution (one-half volume of the ordinary reagent). The solution is now warmed to boiling. The formation of a white precipitate (consisting of calcium oxalate), either in the cold or upon warming, indicates calcium.

The directions given above apply to neutral or faintly ammoniacal solutions of the chlorides of calcium, strontium, and barium. In the ordinary course of a qualitative analysis the precipitated carbonates should be dissolved in a little hydrochloric acid, and the resulting solution evaporated to dryness, warming gently to expel free acid. The residue from this evaporation should be dissolved in 6 to 10 cc. of water, and this solution used for the analysis. The portion to be tested for calcium may be treated with a drop of ammonium hydroxide solution to insure the absence of free acid.

In the use of the above method, particular attention should be given to the following points:—The potassium iodate solution used as a reagent must be fully saturated. This reagent is conveniently prepared by using enough of the dry salt to make a N/2 solution, and allowing it to stand some hours, with occasional shaking. If it is desired to dissolve the salt more quickly by heating to boiling, the warm solution must be cooled to ordinary temperature and agitated before use.

In adding the reagents, particularly the iodate and hydrochloric acid solutions, the amounts added must correspond quite closely with what is called for in the directions given above. The adequacy of these directions has been tested by their employment in analyses of some forty mixtures by myself and others, in the laboratory of the University of Cincinnati. The results obtained were entirely correct.

I desire to express my sincere thanks to Dr. J. F. Snell, whose continued encouragement and suggestions have been invaluable, in this, as in my previously published work.—*Journal of the American Chemical Society*, xxviii., No. 11.

NOTICES OF BOOKS.

Practical Physical Chemistry. By ALEX. FINDLAY, M.A., Ph.D., D.Sc. London, New York, and Bombay Longmans, Green, and Co. 1906.

A FAIRLY elementary text-book of practical physical chemistry has for some time been much wanted, and the author of the "Phase Rule and its Applications" has already given proof of his special qualifications for making the subject interesting and clear. This book quite bears out his high reputation, and will be of the greatest value to

the advanced student. Experimental details are fully described, and as the different chapters are as far as possible independent one of the other, the teacher can quite easily re-arrange the course if it seems desirable to him, and by the time the pupil has worked through the he will have laid a firm foundation in physical chemistry, and will have a much better grasp of the subject than if he had relied upon book knowledge only. The book begins with a chapter of notes on the calculation of results and errors, in reference to which we may point out that the inversion method in contracted multiplication is not generally found the easiest for the student to manipulate with success. In the next chapters on the densities of liquids and gases, the definition of density might with advantage be amended in a subsequent edition. Viscosity, optical measurements, and the distribution law are then considered, when an interesting and instructive series of experiments is described. Electrical methods, conductivity determinations, &c., are treated very fully, and the book as a whole forms an admirable supplement to lecture-work on physical chemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cxliii., No. 25, December 17, 1906.

Report on the Work of M. Grignard (Winner of the Jecker Prize for 1906).—By Henri Moissan.

In 1898, Ph. Barbier was the first to point out that in certain cases magnesium could be advantageously substituted for zinc in Saytzeff's reaction. He thus accomplished the synthesis of dimethylheptenol by treating methyl iodide with natural methylheptenone in presence of magnesium filings. Two years later, M. Grignard resumed the study of this question on the advice of M. Barbier, and he soon discovered that magnesium affords a far greater facility of reaction than zinc, but that in Saytzeff's method it more oftened furnished numerous products of polymerisation. M. Grignard then had recourse to Wagner's plan of preparing the organo-magnesium compound, not by the methods of Löhr, Fleck, and Waga, which experiment had condemned, but by utilising a process already tried by Frankland and Wanklyn for the the organo-zinc combinations. These scientists had observed that in heating methyl iodide with zinc filings in presence of anhydrous ether a volatile product was obtained soluble in ether, possessing the properties of zinc methyl, and apparently corresponding to the formula $Zn(CH_3)_2+O(C_2H_5)_2$. Only the difficulty of conveniently isolating this compound rendered their method inapplicable.

It was to be expected that a metal like magnesium, more electro-positive than zinc and possessing more active affinities, would react more completely and readily; and this result was in fact obtained, for experiment showed that magnesium in presence of an anhydrous ether oxide, and particularly ethyl oxide, attacks the greater number of the halogen ethers even at the ordinary temperature, and furnishes in a total reaction a product soluble in ether.

These organo-magnesium combinations correspond to the general formula RMgX, in which X represents a halogen, and R a monovalent organic radical, fatty, aromatic, polymethylenic, or terpenic. Frequently the presence in this radical of another functional group does not hinder the reaction from being normal. This fact has been established already for the ether oxides of the alcohols (Hamonet), and of the phenols (Bodroux), for α-monobromcamphor (Brühl, Malmgren), iodo-1-hexanone-5 (Zelinski and Moser), for the halogen derivatives of the tri-substituted aromatic amines (Ehrlich and Sachs), and also the mono-substituted (A. Baeyer).

However, the presence of a double bond in the neighbourhood of the halogen atom may render the reaction abnormal, which happens in the case of the bromide and iodide of allyl (Grignard).

Speaking generally, it is the bromine and iodine derivatives which react the most readily; the primary derivatives react better than the secondary and much better than the tertiary (Grignard, Bouveault).

The mixed organo-magnesium compounds are always associated with one or even two molecules of ether (Tschelinzeff). They should probably be regarded as derivatives of oxonium of formula—

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O\!<\!\!\begin{matrix} MgR \\ X \end{matrix} \qquad \text{or} \qquad \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O\!<\!\!\begin{matrix} MgX \\ R \end{matrix}$$

(A. Baeyer and Villiger). (Grignard).

They may be obtained free from ether in a neutral solvent by employing ether or a tertiary amine as catalyser, but in that case they are insoluble.

The ether-organo-magnesium combinations are distinguished by a remarkable facility of reaction. This facility has led to their being substituted in almost all cases (except for the synthesis of allyl alcohols) for the organo-zinc compounds, with great advantage from the point of view of rapidity, and yield a number of the reactions. These compounds have also enabled the institution of a certain number of new methods for which the zinc compounds are altogether inapplicable.

Altogether about 350 memoranda of the organo-magnesium compounds and their applications have been published. The most important will be mentioned, with a survey of their principal properties.

All the compounds which possess a movable hydrogen atom, water, acetylene carbides, alcohols, phenols, acids, ammonias, amines, amides, imides, electro-negative compounds with the group CH_2, &c., exchange this hydrogen atom with the MgX derivative with the formation of a hydrocarbide, RH (Grignard and Tissier, Mermier, Houben, &c.). In particular, the true acetylene compounds, $R'.C\equiv CMgX$, possess all the properties of the other organo-magnesium products (Jotsitch).

It is to the synthesis of alcohols that the new organo-metallic compounds have most richly contributed. Oxygen oxidises them into alcohols or phenols (Bodroux, Bouveault, Zelinski). The aldehydes, ketones, ether-salts, chlorides, and anhydrides of acids lead generally with good returns to primary, secondary, or tertiary alcohols, as the case may be (Grignard, Grignard and Tissier).

The methods of synthesis of the aldehydes have been largely revised; we may quote the use of the formic ethers at -50° (Gattermann and Maffezoli), of ethyl orthoformiate (Tschitschibabin, Bodroux, Moureu, and Delange), of the di-substituted formamides (Bouveault), and of the carbylamines (Sachs and Levy), as well as the indirect products of MM. Behal and Sommelet connected with certain ether-oxides of α-glycols.

The case is the same for the synthesis of ketones by the action of the nitriles (Blaise), the imides (Béis), the anhydrides of acids at -20° (Fournier).

We may add that the presence in the same molecule, of several replaceable functional groups does not, in general, hinder the reactions from proceeding normally, either simultaneously if all the groups are identical, or successively if the groups are not equally electro-negative. Thus, the diketones, except the β-diketones (Valeur, Zelinski), the ethers of dibasic acids (Valeur), give, in general, bi-tertiary glycols, the aldehydic or ketonic alcohols give glycols (Tiffeneau, Franke and Cohn); the ketone ethers, except the β, the chloride of ethyloxalyl, give rise to the alcohol acids (Grignard), and cyanacetic ether to the β-ketonic ethers (Blaise).

The direct fixation of the carbonic anhydride upon the magnesium derivative furnishes a method of synthesis of acids often preferable to the employment of potassium cyanide (Grignard, Houben and Kesselkaul, Zelinski, Jotsitch).

It is worthy of note that these organo-magnesium compounds possess the property of uniting with the double bonds of the aromatic ketones to give rise to substituted saturated compounds (Kohler, A. Haller and E. Bauer).

Finally the organo-magnesium compounds can combine with halogen organic bodies, producing by elimination of the mineral part, either hydrocarbons (Houben, Tiffeneau), or more complex compounds (Hamonet, Grignard). The action of ethylene monochlorhydrin, in particular, has enabled the carrying out of the only regular method of synthesis of the primary arylethyl alcohols (Grignard).

An analogous process with the halogen derivatives of the metals or metalloids has furnished a whole series of organo-metallic compounds of tin (Pope and Peachey), antimony, lead, mercury (Pfeiffer and his pupils) thallium (Meyer and Bertheim), silicon (Kipping, Dilthey and Eduardoff), phosphorus and arsenic (Auger and de Billy, Sauvage).

To complete the account, mention must be made of many interesting researches upon iodine, sulphur, selenium, sulphurous anhydride, carbon sulphide and oxysulphide, phosgene, the quinones, the ketone ethers of active alcohols, the magnesium derivatives of alcohols, amines, &c.

These numerous examples abundantly testify to the value and fertility of the reaction that chemists have, with justice, called the *Grignard reaction*.

Lavoisier Medal.—Report of M. Berthelot.

This medal is awarded by the Bureau de l'Académie to S. M. Jörgensen.

The first researches of S. M. Jörgensen on the periodides of the alkaloids were published in 1867. These experiments led him to the discovery of a tri-iodide of potassium, then of a hexaiodide of mercury, and finally of the double periodides of thallium and of the ammoniated and phosphuretted bases.

Since then, he has devoted himself entirely to the study of the ammonium metallic bases.

Continuing and extending the researches of Frémy and Blomstrand, he carried on his investigations successively upon the series of the yellow, pink, and purple salts of cobalt, chromium, and rhodium. He demonstrated how these could be recognised and how one could pass from one series to the other. These researches were completed later by the cryoscopic investigations of M. Petersen.

To these important series there have been added researches upon the xanthochromic salts, rhodosochromic salts, platinic acid and its curious compounds.

For the importance of his results, S. M. Jörgensen certainly takes the first place in this special branch of chemistry, the ammonium metallic bases, to which so many chemists have turned their attention. He has co-ordinated and classified all the series, or nearly so, for the trivalent metals. In the latter years he has brought much matter to the difficult study of the platinum bases.

The purity of the purple salts of rhodium has enabled him to prepare this metal under quite new conditions, and to determine thence its atomic weight.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Society of Chemical Industry, 8. "Sixth International Congress of Applied Chemistry at Rome," by W. F. Reid.

TUESDAY, 8th.—Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Signalling to a Distance, from Primitive Man to Radio-telegraphy" (Experimentally Illustrated), by W. Duddell, M.Inst.E.E.

WEDNESDAY, 9th.—Society of Arts, 5. (Juvenile Lecture). "Perils and Adventures Underground," by Bennett H. Brough.

GOVERNMENT GRANT to defray the expenses of Scientific Investigations. Applications for the year 1907 must be received at the Offices of the Royal Society not later than JANUARY 31st next, and must be made upon printed forms to be obtained from the Clerk to the Government Grant Committee, Royal Society, Burlington House, London, W.

JUNIOR Assistant wanted in Analytical Laboratory. One with knowledge of Brewing Analysis preferred. State experience, &c.—Apply, 20, Kilvert's Buildings, Withy Grove, Manchester.

REQUIRED, Assistant Analyst for Public Laboratory. Organic experience essential. State experience, present position, and salary.—Address, "Chemist," CHEMICAL News Office, 16, Newcastle Street, Farringdon Street, London, E.C.

WANTED, Chemist with knowledge of Paint Manufacture.—Address, P. M., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

WANTED in the Laboratory of a large Manufacturing Firm who employ several Chemists, a Young Man thoroughly trained in systematic Chemistry (Organic and Inorganic) and in the Technology of Chemical Processes, to learn the routine work of the Laboratory, assist the Chief Chemist, and conduct original investigations. State age, training, experience, and salary expected.—Address, S. C., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

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Mr. J. F. BRIGGS.

A COURSE of TWELVE LECTURES, followed by Laboratory Work, will be given on MONDAY EVENINGS from 7.30 to 9.45, commencing MONDAY, JANUARY 7th, 1907. Lecture, 7.30 to 8.30; Laboratory, 8.30 to 9.45.
The Syllabus includes the Analysis of Paper and Pulp, including the Strength and Thickness of Paper, determinations of Mechanical Wood, Moisture, Ash, Loading; Microscopic Tests and approximate Determination of Fibres.
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COURSES of INSTRUCTION are given in the BACTERIOLOGY of FERMENTATION, &c., suitable for Candidates for the Institute of Chemistry Examinations.
An EVENING CLASS in BACTERIOLOGY will commence on MONDAY, JANUARY 7th.
For particulars apply to the SECRETARY or to Prof. HEWLETT.

CITY AND GUILDS OF LONDON INSTITUTE.
SALTERS' COMPANY'S RESEARCH FELLOWSHIP.

The Research Fellowship founded by the Salters' Company for the encouragement of Higher Research in Chemistry in its Relation to Manufactures, tenable at the City and Guilds Central Technical College, being now vacant, the Executive Committee of the Institute are prepared to receive applications from Candidates. The grant made by the Company to the Institute for this purpose is £150 a year. Copies of the Scheme under which the Fellowship is awarded may be had from the HONORARY SECRETARY of the City and Guilds of London Institute, Gresham College, Basinghall Street, E.C.
JOHN WATNEY, Honorary Secretary.

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CALCIUM AS AN ABSORBENT OF GASES FOR THE PRODUCTION OF HIGH VACUA AND SPECTROSCOPIC RESEARCH.*

By FREDERICK SODDY, M.A., Lecturer in Physical Chemistry in the University of Glasgow.

I. *Introductory.*

This paper contains an account of researches carried out by the aid of an electric furnace designed to heat reagents in soft glass tubes up to temperatures far above the softening point of glass, and has special reference to the use of calcium under these conditions as a valuable absorbent of gases. Recent work on the generation of helium from the radio-elements has shown the necessity for more simple, certain, and powerful means of absorbing other gases and in particular nitrogen. The usual practice of Sir W. Ramsay and the writer when working together was to make provision for the removal of compounds of hydrogen, oxygen, and carbon, but to take the utmost precautions against the admission of air into the apparatus in the first place. If nitrogen was present in spite of the precautions taken, it was often possible, by gently running the spectrum-tube, to absorb it by the hot electrodes of aluminium, the lines of helium, if present, appearing as the nitrogen spectrum faded.

The difficulty in absorbing nitrogen is that the usual absorbents, for example, a mixture of lime and magnesium, only react above the softening temperature of an exhausted soft glass tube, and the present researches had their origin in an attempt to enable higher temperatures and more powerful absorbents of gases to be used within soft glass apparatus. Lithium, it is true, absorbs nitrogen at a very low temperature, but its use introduces hydrogen. A good example of a very perfect train of absorbents, able to absorb all known gases with the exception of those of the argon family, is to be found in the recent researches of Debierne on the production of helium from radium and actinium (*Comptes Rendus*, 1905, cxli., p. 383). "Oxygen is absorbed by heated copper; the absorption of hydrogen is secured by the action of heated copper oxide and phosphorus pentoxide, at the same time the copper oxide transforms gaseous carbon compounds into carbon dioxide, which is absorbed by potash, and finally nitrogen is absorbed by pure lithium."

Now such an apparatus serves but one experiment, and has to be built up afresh for each, because it is necessary to fill it after the absorption with mercury in order to compress the helium sufficiently to detect it. The labour involved during a lengthy investigation may be imagined. It is therefore very satisfactory to be able to state that I have found that a single reagent, namely, calcium, at the high temperature attainable by the use of my furnace, would serve instead of all the reagents employed by Debierne, and do the work far more effectively and rapidly. Calcium, under the conditions mentioned, is a universal absorbent of all gases with the exception of the argon group.

II. *Historical.*

Till recently calcium has been a very uncommon metal, while barium and strontium still belong to the category of chemical curiosities. Maquenne (*Comptes Rendus*, 1892, cxiv., p. 225), found that when amalgams of these three metals were heated in nitrogen, the mercury was volatilised and nitrides of the metals were formed. The absorption took place at a lower temperature than in the case of the metals magnesium and aluminium. Barium was stated to lend itself best to the experiment. None of the alkaline-earth metals were investigated by Lord Rayleigh and Sir W. Ramsay in their examination of the known absorbents of nitrogen (*Phil. Trans.*, 1895, clxxxvi., A, p. 187) on account of the difficulties in obtaining large quantities of these metals at that time. After the discovery of argon, Maquenne (*Comptes Rendus*, 1895, cxxi., p. 1147) showed that a mixture of calcium oxide and magnesium rapidly absorbed the oxygen and nitrogen of the air when heated in a hard glass tube, and attributed this reaction to the production of calcium in an extremely divided state. He states that a monometer attached to the apparatus showed a diminution of pressure from the atmospheric equal to 70 and even 73 cm. of mercury. This mixture is now commonly employed in the preparation of argon, and it is customary to accept Maquenne's explanation of its absorbing power. It is, however, quite certain that the commercial calcium in the form of compact metal bars, produced by electrolysis, behaves in a manner entirely different from the "nascent calcium," if such it be, produced by heating a magnesium and lime mixture; for the former, heated in a tube filled with air at atmospheric pressure, produces no noticeable absorption, even at the highest temperatures.

Moissan first succeeded in preparing calcium in quantity sufficient to make an accurate study of its proportion (*Comptes Rendus*, 1898, cxxvi., p. 1757, and cxxvii., pp. 29, 497, and 584). His calcium was in finely divided crystalline condition, and was obtained by acting upon calcium iodide with excess of sodium. The calcium is deposited out from the sodium on solidification, and the latter is removed by the action of absolute alcohol, which does not attack calcium. He showed that at a dull red heat this calcium absorbs both hydrogen and nitrogen with incandescence, forming nitride and hydride respectively. The hydride heated to the softening temperature of a Bohemian glass tube in an atmosphere of hydrogen neither absorbed nor evolved gas. In a determination of its melting-point the calcium was heated in a vacuum obtained by the use of a mercury pump. Moissan noted the evolution of small quantities of gas which were pumped off, "but as soon as the metal became dull red hot the last traces of gas are absorbed, and the vacuum stood at 1 mm." This inconsistency might have been due to sticktion of the mercury in the guage, or to an error in its reading, for, as Moissan himself remarks, the last traces of gas are absorbed under these conditions.

Calcium, electrolytically produced in the form of compact bars, free from mercury and oil, has been available for over two years, and has been the subject of much interest. Those who have examined it must have been more struck with its apparent disinclination to react than with any exceptional reactivity. Thus the attempts to replace the magnesium or magnesium-lime mixture by this calcium in the preparation of argon have never succeeded in my experience. Even when heated to 1200° C. in an electric oven it refuses, after a very slight initial action, to absorb nitrogen. It must be heated to a very high temperature in the blowpipe before it ignites in the air, and then readily goes out. In one experiment a powerful arc was caused to pass between calcium points in air without inducing combustion.* Negative results of this character could be multiplied.

Arndt undertook a research on the melting-point of commercial calcium (*Ber.*, 1904, xxxvii., p. 4733), in which the

* Read before the Royal Society, November 15th, 1906. (An abstract of this Paper appeared in Chemical News, vol. xciv., p. 305).

* This, however, is partly due to the extraordinarily slight heating which electrodes of calcium experience when a discharge is passed through a gas between them. Of all metals calcium heats the least, and is in this respect far superior to aluminium. But for other difficulties it might be used to replace aluminium, with advantage, as the electrodes of vacuum tubes in the case of the inert gases. A steady arc can be maintained between calcium points in air with a very small ampérage.

metal was heated as in Moissan's experiment in a vacuum of 1 mm. pressure to avoid chemical action. He noticed that the calcium began to volatilise below its melting-point, and that the vapour reacted energetically with the residual air, so that the pressure on the manometer sank to an unreadable value. Absorption commenced at 700° C., was rapid and accompanied by visible volatilisation at 730°, whereas the melting-point was found to be 800°. When a Plücker spectrum tube was included, it was found that "the nitrogen spectrum faded rapidly, while the lines of hydrogen (from a trace of water present) remained behind with the lines of argon." He found that the vapour of magnesium did not exhibit nearly the absorptive power of calcium.

With the use of the apparatus to be described I arrived independently at, and have confirmed, the observation of Arndt on the extreme rapidity of absorption of the oxygen and nitrogen of air by the vapour of calcium. In addition I have found that all the common gases can be absorbed equally well, although in some cases, as the above quotation from Arndt's paper shows for hydrogen, complete absorption is not effected by simple heating alone.

III. *Electric Furnace for strongly Heating Reagents in Glass Vessels.*

The apparatus usually employed depends upon the internal heating of the reagent by an electric resistance circuit and the protection of the glass walls by a screen of porcelain placed between it and the enclosed furnace. It is shown to the scale of 6 inches to the foot in section in Fig. 1. Figs. 2, 3, 4 are transverse sections on the lines *x*, *y*, *z* respectively. The outer containing vessel is made out of soft glass tubing, and is in two parts, the upper B and the lower B_2, which are ground to fit together accurately at D. The lower part B_2 has two mercury cups with platinum wires b_2 sealed through the glass. The upper part B widens at the shoulder *d*, on which rests the porcelain shield-tube K. This is slipped into the tube, which is then constricted at A and joined to a narrow piece of tubing for connecting to other apparatus. The furnace tube J, which carries the heating wire, slides through the ground-joint of B and passes inside the shield-tube K. For the upper part of its length it is grooved with an external screw thread of about 1 mm. pitch, and wound with a platinum wire *ii* of 0·25 mm. diameter. It passes through the holes *jj* into the inside of the tube, and is joined to stouter leads of nickel, copper, or platinum, or is simply doubled on itself. The leads pass through the doubly-bored porcelain insulator I, which slips within the lower half of the furnace tube and the upper part of B_2, and are finally taken into the mercury cups. The lower end of the furnace-tube J rests on, and is supported by, the upper end of B_2, and itself surrounds and supports at its upper end a porcelain test-tube L, in which the reagent to be heated is placed at C.

The whole arrangement is readily taken to pieces at the ground-joint D, for re-charging, cleaning, or repairs. The end B_2 usually carries between the two mercury cups a narrow tube, shown by dotted lines, to which is attached a bulb and tap, shown in Fig. 5, for the purpose of admitting mercury into the apparatus without introducing air, and also for conveniently filling the mercury cups and other purposes. An oil or mercury seal may surround the ground-joint, but it is not necessary if it is of good workmanship.

For special work, where the possibility of leaks or the the presence of vapour of grease is to be avoided, it is easy to dispense with the ground-joint D and to make the apparatus in one piece. In this case B is made long so that it can be repeatedly opened and sealed, and the various parts are introduced through the upper end by suitable tongs. But these refinements are usually quite unnecessary if the ground-joint is of good workmanship and is well lubricated, and if the leads are of sufficient conductivity not to heat the joint. In special work, too, the mercury cups may be dispensed with and the wires continued through the glass seal if the presence of mercury vapour is to be avoided.

[*Added*, Nov. 20.—An improved and thoroughly satisfactory method of working, applicable whether the ground-joint is used or not, is to dispense with the porcelain insulator I, and to bore two holes opposite each other at the lower end of the furnace tube J, twisting one end of the doubled platinum heating wire through each hole together with a length of "flexible" copper wire, and continuing the two

Fig. 1.

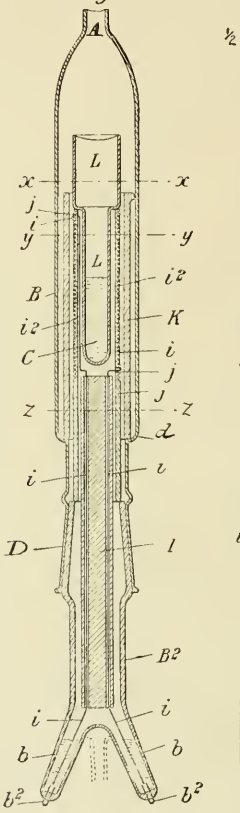


Fig. 2

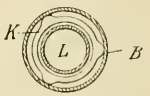


Fig. 3.

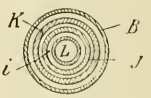


Fig. 4.

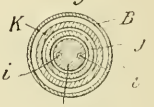
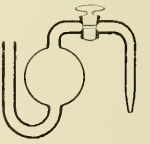


Fig. 5.



flexibles, insulated if necessary in little glass tubes, into the cups *bb*, where they make good touching contact with the platinum, without the use of mercury. In this way a mechanically strong joint with the fine heating wire is secured, the presence of mercury inside the vacuum is altogether avoided, and the formation prevented of a mercury arc between the two cups when a high tension discharge is passed through the vacuum, which in the first form of apparatus constituted an occasional source of annoyance and damage.]

With this apparatus reagents may be safely heated to temperatures far above the melting-point of glass without injuring the apparatus. After nearly two years' use of these furnaces I do not recall a single case where the heat has caused the glass to crack or break while in use, although, of course, the glass tends to get brittle and to break when being cleaned more readily after use than before. If required for prolonged heating at high temperature it is an advantage to blow a bulb on the tube at the hottest part of the furnace, otherwise, when the porcelain shield-tube has become heated through, the glass is apt to melt. These shield-tubes never break. The furnace-tubes are more fragile but stand extremely well, while, of course, the test-tubes containing the reagents require the most frequent replacement. Tubes made of thin iron would for many purposes have very many advantages over porcelain. But they must be gas-tight at the lower end, for the vapour of calcium would ruin the platinum wire if it came in contact with it.

The limit of temperature attainable in this apparatus is fixed mainly by the volatility of the heating wire in the high vacuum usually maintained within the apparatus, and for this reason platinum or one of its alloys must be used. Iron or nickel volatilise and the wire is destroyed in a few minutes. Even with platinum the volatilisation of the metal is serious at a bright-red heat. In addition, a certain tendency to become brittle with loss of metallic qualities, which is noticeable in ordinary platinum resistance furnaces, thermometers, and thermocouples, and which prevents their prolonged use at temperatures above 1200° C., appears to be far more marked and to take place at lower temperatures in the high vacuum, rendering occasional re-windings of the furnace necessary. The cause of this has not been fully explained. An examination of somewhat analogous phenomena in the case of nickel has been recently made by Dr. H. C. H. Carpenter in a paper read before Section G of the British Association, 1906, and attributed by him to gases in the nickel (*Engineering*, August 17, 1906, p. 222). I am inclined to connect the phenomenon in the case of platinum with the vaporisation of the metal. If tantalum wire could be obtained, no doubt it would prove far more suitable than platinum. Naturally, a high vacuum within the apparatus tends greatly to conserve the heat and to diminish convection, and the risk of the outer vessel melting. In this respect the apparatus is the antithesis of the Dewar vessel for storing liquid air.

IV. *Absorption of Gases by Calcium.*

If the apparatus described, charged with a small piece of calcium, and furnished with a Plücker spectrum-tube, is exhausted by a Fleuss pump, and the furnace heated, gases, consisting of compounds of hydrogen, carbon, and oxygen, are given out by the calcium. If connection with the pump is then shut off and the heating continued, absorption of the remaining gases, accompanied by volatilisation of the calcium, takes place, and the vacuum rises almost instantly to a point at which no discharge can be passed through the spectrum-tube. By a non-conducting vacuum is to be understood one of greater resistance than an alternative spark gap in air of 2 to 3 cm., unless the length of the gap is given.

If air is introduced into the apparatus, all but argon is rapidly absorbed, and quantities up to 10 or 20 cc. can be thus dealt with. These experiments with air are, however, of interest from so many points of view that they will be dealt with in detail later.

In a similar way it was shown that carbon monoxide, carbon dioxide, water vapour, hydrogen, acetylene, sulphur dioxide, ammonia, and the oxides of nitrogen (nitric oxide, with deflagration of the calcium) are all as readily and completely absorbed as in the case of the oxygen and nitrogen of the air. Quantities of the several cubic centimetres disappear within a minute after introduction, and the vacuum-tube becomes non-conducting.

Finally, in order to put the power of the calcium to as severe a test as possible, several successive quantities of coal-gas, each of several cubic centimetres, were introduced into the apparatus after the absorption temperature had been attained. Within a minute after each addition the spectrum-tube became non-conducting to the discharge. Calcium thus acts as a universal absorber of chemically valent gases.

The case of hydrogen and its compounds alone calls for fuller treatment, for at too high temperature calcium hydride possesses an appreciable tension of dissociation. The same is of course true of calcium carbonate, but this compound does not appear to be formed when only small amounts of carbon dioxide are absorbed by the calcium. If hydrogen or its compounds are present in a gas in large quantity, the spectrum-tube, after the absorption of the other gases, shows still the hydrogen lines, and refuses to become non-conducting as long as the temperature of the furnace is maintained. But if the heat is reduced the non-conducting stage is reached at once. In one experiment 1 cc. of hydrogen was introduced, and the heat reduced. The spectrum-tube became non-conducting in forty seconds.

Careful experiments have shown that even after cooling an infinitesimal quantity of hydrogen remains unabsorbed. Thus if, after cooling, mercury is allowed to fill the apparatus and compress the residual gas many hundred times into a tiny spectrum-tube, a very faint hydrogen spectrum can be seen, although the spectrum-tube, even after this concentration of the gas, is still of high resistance and fluoresces brilliantly under the discharge. This residual trace will be shown to be of great value in certain experiments.

A point of very great practical importance arises out of the dissociation phenomena of calcium hydride. Different commercial specimens of electrolytic calcium exhibit differences in their behaviour which I have traced to the presence of hydride in some specimens and not in others. The presence of this hydride quite alters the characteristics of the absorption process, and although with sufficient experience it is possible to get good results in spite of the presence of hydride, this experience is apt to be dearly bought. When hydrogen is present the real absorption temperature is apt to be overstepped, for instead of a non-conducting vacuum being obtained, as it should be almost instantly with a proper specimen of metal, the dissociation tension of the hydrogen is sufficient to enable the discharge to pass. An inexperienced operator or one accustomed only to the character of the purer metal, will, in consequence, continually increase the temperature, and the tension of the hydrogen of course increases, and may ultimately become quite measurable on a guage. Before it is realised that the proper temperature has been far overstepped, the metal may have melted, subsequently to crack the crucible on cooling, the platinum wire may fuse or volatilise, and even the glass envelope may soften. Whereas, if instead of increasing the temperature, the heat had been cut off, the non-conducting stage would have been reached in a few seconds. It was noticeable that of two specimens, one excellent and the other containing hydrogen and unsuitable, the latter was by far the more malleable and could be always detected by this test after it had accidentally got mixed with the other specimen. But this difference of properties may not have been due to the presence of the hydride. No one would use metal containing hydride wittingly, but it is well to know that by cutting off the heat, when the spectrum of the gas becomes that of hydrogen, quite satisfactory results are attainable. But the sacrifice of time and apparatus, destroyed by excessive temperature, was considerable before the differences between the specimens of metal were suspected and the differences of behaviour understood.

Experiments were tried to see if calcium which had been strongly heated and allowed to cool in an atmosphere of helium and argon, respectively, re-evolved any trace of these gases when re-heated *in vacuo*, but in each case with negative results.

(To be continued).

AN EXAMINATION OF THE LIGHTER CONSTITUENTS OF AIR.*

By JOSEPH EDWARD COATES, B.Sc. (Wales).

THIS research was undertaken with the object of ascertaining whether a large quantity of air, if systematically fractionated, would yield any constituent lighter than helium. It has been stated that "coronium" has revealed its presence in the gases emitted from the Solfatara of Pozzuoli by a line of wave-length 531·5—531·6; and that from some of the Vesuvian fumaroles gases have been obtained which give rise to new lines not coincident with any important lines in the neon or helium spectra (Nasini, Anderlini, and Salvadori, *Accad. dei Lincei*, 1898, vii., p. 73). Again, it has been stated in a lecture delivered at the Royal Institution (April 11, 1902), that the most volatile part of the atmosphere contains constituents showing many unknown lines (Dewar). Since that date, however, no further account of such substances has appeared.

Another object of the present research was to determine the proportion of free hydrogen in air by the method of fractionation. The most important estimations have been made by Gautier, Rayleigh, and Dewar. Gautier, using the method of passing air over red-hot copper oxide, found 19·5 volumes of free hydrogen in 100,000 volumes of air, *i.e.*, about half as much free hydrogen as carbon dioxide (*Ann. Chim. Phys.*, 1901, xxii.). Rayleigh (*Phil. Mag.*, 1902, iii., p. 416) discussed, and, in part, repeated the work of Gautier; he considered three parts per 100,000 as a maximum estimate, but regarded the question as still unsettled. Dewar, in the lecture mentioned above, stated that 100,000 parts of air contain not more than one part of hydrogen.

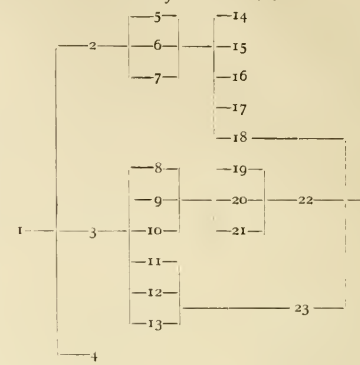
The conclusions arrived at in this paper may be briefly stated:—(1) There are no unknown lines in the spectrum of the lightest portions of the air, all those observed being traceable to helium, neon, and hydrogen; (2) the amount of hydrogen separable from air is much less than that given by the above-mentioned investigators, for it amounts to about one volume per million and a-half volumes of air.

The first stage in the fractionation was effected by means of the air-liquefying apparatus at University College, Gower Street. The air of the compressor room (situated in the basement and well ventilated) passed through the apparatus, and the portion which did not liquefy was collected in a large gas-holder. This, together with fresh supplies of air, was repeatedly circulated through the apparatus, with the object of making a preliminary concentration of the lighter portions. To avoid contamination with hydrogen, the gas-holder was well painted inside, and the compressor cylinders lubricated with very dilute alkali. The total quantity of air dealt with in this operation amounted to about 73,500 litres.

A second fractionation of the gas thus collected was obtained by liquefying about 70 or 80 litres at a time in a glass bulb immersed in liquid air boiling under reduced pressure. (A description of this piece of apparatus and its uses has been given by Ramsay and Travers, *Phil. Trans.*, 1901, cxcvii., A, p. 58). Light fractions were boiled off, and the process repeated several times until the volume was reduced to 4700 cc. This portion (1) was separated, by the method of absorption in cooled charcoal, into three fractions, (2) not absorbed at about −190° C., (3) not absorbed at about −110° C., (4) discarded. Spectroscopic examination showed (2) to be almost pure neon and helium with faint hydrogen lines. An attempt was made to fractionate (2) and (3) at the temperature of liquid air boiling at ordinary pressure (−190° C.), but, in the case of (3), the fractions always showed the nitrogen spectrum (see table of fractionations): it was therefore decided to work at the temperature of liquid air boiling under reduced pressure, which represents a temperature about −205° C.

* A Paper read before the Royal Society, December 13, 1906.

Table of Fractionations.



Speectroscopic examination showed (5) and (6) to be chiefly neon and helium, with a little hydrogen—no new lines were detected; (7) was neon and nitrogen, while (8) and (11) consisted chiefly of nitrogen; (5), (6), and (7) were mixed and separated into the fractions; (14) pumped off at −205° C., (15) at −190° C., (16) and (17) at 18° C., and (18) at 236° C.; (8), (9), (10) were mixed, and similarly separated into fractions (19), (20), (21); (19) gave the nitrogen spectrum, (14), and (15) consisted of neon and helium; (16) and (17) contained hydrogen in addition to neon and helium, while (18) contained more nitrogen than neon. Fractions (14), (15), (16), (17) were therefore analysed for hydrogen, whilst the remaining fractions, as shown by the table, were worked up for neon and helium, of which 25 cc. were obtained. The gases were measured separately, sparked with oxygen, the excess of which was subsequently withdrawn by means of phosphorus. The diminution in volume gave the amount of hydrogen present. The gases were measured by the method described by Ramsay (*Roy. Soc. Proc.*, lxxvi., A, p. 113).

	Cc.		Cc.
Volume of (14)	1·258	Volume of (15)	1·995
„ after sparking	1·260	„ after sparking	2·001
„ of hydrogen .	Nil	„ of hydrogen .	Nil

N.B.—The slight increase in volume represents a small error of measurement of the order about 1 in 400.

	Cc.		Cc.
Vol. of (16)	11·615	Volume of (17)	6·507
„ after sparking..	11·420	„ after sparking	5·924
„ of hydrogen ..	0·195	„ of hydrogen .	0·583

Total volume of hydrogen .. 0·778 cc.

The spectra of (14) (15), (16), (17) were very carefully compared with the spectrum of a neon and helium tube, and they agreed exactly throughout; no new lines could be detected; this also shows that the contractions could not have been due to the presence of carbon monoxide, possibly derived from the charcoal. Any hydrocarbons in the air would have been removed in the charcoal.

As a test of this method of separating a small proportion of hydrogen from air, a parallel series of fractionations was performed on about 60 litres of air, to which 5·6 cc. (measured to 0·1 cc.) of hydrogen had been added. Three fractions were finally obtained from charcoal:—(1) At −205° C., (2) and (3) at −190° C. Analysis, as before, gave the following results:—

1.	4·602 cc. gave 0·170 cc. hydrogen	(3·7 per cent)	
2.	13·005 „ 0·702	„	(5·4 „)
3.	29·259 „ 1·585	„	(5·4 „)

Total volume of hydrogen .. 2·457 cc.

Thus, only about half the added hydrogen was recovered. The most probable source of loss seems to be in the fractionation from the liquefied gas, when even the passage of air bubbles through the liquid appears insufficient to expel all the hydrogen. Dewar (*loc. cit.*) has also stated that hydrogen is very soluble in liquid air; it is thus possible that a little hydrogen might have been removed during the initial process with the liquefying machine. It is noteworthy that the fraction pumped from the charcoal at -205° C. contains less hydrogen than that which comes off at -190° C.; the absorption of hydrogen seems to be of about the same order as that of neon.

The total volume of hydrogen obtained from the air was 0·778 cc., and the total volume of mixed neon and helium was 46 cc. Using the estimate of Ramsay (*loc. cit.*) and of Dewar (*loc. cit.*), viz., 60,000 volumes of air contain 1 volume of combined neon and helium, it is found that 2,760,000 cc. of air contain 46 cc. of neon and helium and 0·778 cc. of hydrogen, whence 3,550,000 cc. of air contains 1 cc. of hydrogen. This number can be corrected by assuming, as an approximate factor, the ratio 2·5/5·6 derived from the experiments on the air to which hydrogen had been introduced. The corrected estimate is 1 cc. of hydrogen in 1,583,600 cc. of air, or, approximately, one volume of hydrogen per million and a-half volumes of air.

On comparing the total volume of air originally dealt with, it is evident that the liquefying plant was of very little use in concentrating the lightest portions; it is certainly better to calculate the hydrogen on the quantity of neon and helium actually obtained than on the original volume of air.

It appears from these results that the proportion of free hydrogen in the atmosphere is exceedingly small—so small, indeed, as to make its exact estimation a matter of extreme difficulty, and we must regard our results as indicating the order rather than the exact proportion in which the hydrogen is present.

In conclusion, I wish to express my warmest thanks to Sir William Rsmsay, who suggested and constantly superintended the work during its progress.

DETERMINATION OF URANIUM AND VANADIUM.

By A. N. FINN.

A study of the ore carnotite, which is a potassium uranyl vanadate, repeatedly required the determination of uranium and vanadium. This led to a comparison of the various titration methods that have been suggested.

Belohoubek (*Journ. Prakt. Chem.*, xcix., 231) refers to the reduction of uranium in solution by zinc and sulphuric acid, and titration with potassium permanganate. Sutton, in the sixth edition of his "Volumetric Analysis," states that this method is very accurate if care is taken to insure complete reduction, which requires from one-quarter to one-half an hour.

Determinations of uranium by this method in solutions of uranyl sulphate gave very satisfactory results provided the potassium permanganate solution was not more than twentieth-normal. When, however, uranium is to be determined from a complex mixture or an ore, great difficulty is found in securing the uranium in a form sufficiently pure for the titration. This is especially true in the presence of vanadium.

The general method of separating the uranium and vanadium from each other, and from the various other elements in the ore, is to treat an acid solution of the ore with an excess of sodium carbonate, which precipitates the iron, aluminium, &c., and filter. The filtrate containing the uranium and vanadium is acidified, the carbon dioxide expelled by boiling, and the solution is made alkaline with sodium, potassium, or ammonium hydroxide. This precipitates the uranium as the corresponding uranate, while the vanadium remains in solution. The uranate is dissolved in sulphuric acid, reduced with zinc, and titrated with permanganate. The solution of vanadium is acidified, reduced with sulphur dioxide, and titrated with permanganate.

The precipitated uranate is gelatinous, and it was found impossible to wash this precipitate free from vanadium, and since the uranate is slightly soluble it is not desirable to wash or re-dissolve it many times.

In view of this fact, it became necessary to find an accurate and, if possible, a quicker method for the separation and determination of uranium and vanadium.

This was accomplished by precipitating the uranium in alkaline solution as a phosphate. This precipitate, ammonium uranyl phosphate, is not gelatinous, is insoluble, and may easily be washed free from vanadium.

To show that the volumetric method of titrating the reduced solutions with permanganate is consistent in itself, samples of uranium salts containing no vanadium were used, and the following results were obtained:—

Sample.	Grms.	Per cent U_3O_8.
Solution No. I. ..	9·5058	3·195
	5·1820	3·120
	5·0603	3·167
	5·1570	3·135
Solution No. II. ..	10·2941	5·084
	10·2839	5·056
Solution No. III. ..	11·7228	5·228
	4·4641	5·276

Samples of solution No. III. precipitated with ammonia, ignited and weighed as U_3O_8, gave the following results:—

Grms.	Per cent U_3O_8.
3·81955	5·237
5·3409	5·297

For vanadium, material free from uranium was used, and the following results obtained:—

Sample.	Grms.	Per cent V_2O_5.
Solution No. IV. ..	10·7412	0·945
	10·4142	0·946
	11·3310	0·941
	11·4935	0·947
Solution No. V. ..	12·8359	1·338
	12·6929	1·340
	15·2051	1·349
	14·1954	1·339
Solution No. VI. ..	0·3311	39·127
	0·4341	39·170
	0·3004	39·200

The method suggested for determining uranium and vanadium is, in detail, as follows:—

Dissolve a sample of ore that does not contain more than 0·25 grm. of U_3O_8 in sulphuric acid (1:5), and evaporate to fumes of the acid. Cool, dilute, add an excess of sodium carbonate, and boil until the precipitate settles well. Filter, and wash with hot water. Dissolve the precipitate in the smallest possible amount of sulphuric acid, dilute, add an excess of sodium carbonate, boil, filter, and wash. Acidify the combined filtrates and washwaters with sulphuric acid. Add ammonium phosphate (0·5 grm. is usually sufficient), heat to boiling, and make alkaline with ammonia, boil for a few minutes, filter, and wash with hot water containing a little ammonium sulphate, which prevents the finely divided particles of the precipitate from passing through the paper.

The filtrate now contains the vanadium and the precipitate the uranium. Acidify the filtrate with sulphuric acid, pass sulphur dioxide into it until it becomes blue, boil to expel the excess of sulphur dioxide, and titrate while hot with permanganate. The iron factor of the per-

manganate solution multiplied by 1·631 gives the V_2O_5 factor, or by 0·9159 gives the vanadium factor.

Dissolve the ammonium uranyl phosphate in sulphuric acid, add some granulated zinc, and let the action continue vigorously for at least thirty minutes. Remove the undissolved zinc by filtering over asbestos, using a suction pump, and titrate at about 60° with permanganate (twentieth-normal).

The iron factor of the permanganate solution multiplied by 2·5167 gives the U_3O_8 factor, or by 2·133 gives the uranium factor.

By this method of separation, reducing the solutions, and titrating with permanganate, the following results were obtained :—

Sample.	Grms.	Per cent U_3O_8.	Per cent V_2O_5.
Solution No. VII. ..	10·7904	1·074	1·429
	21·5602	1·068	—
	15·0921	1·085	1·407
	10·6119	1·063	1·415
Ore-carnotite I. ..	1·0002	11·793	6·363
	1·0013	—	6·300
	1·0004	11·885	6·261
Ore-carnotite II. ..	1·0009	6·755	6·849
	2·0005	6·702	6·526
Ore-carnotite III. ..	1·0006	4·873	5·128
	1·0003	4·945	5·358
Ore-carnotite IV. ..	1·00045	1·834	—
	1·00025	1·728	—
Ore-carnotite V. ..	0·9994	0·4094	—
	1·2004	0·4205	—

—*Journal of the American Chemical Society*, xxviii., No. 10.

THE OPTICAL ROTATION OF GLIADIN IN CERTAIN ORGANIC SOLVENTS.

By W. E. MATHEWSON.

THE experiments given here were carried out in connection with an investigation, the object of which was to effect some improvement on the present methods of flour analysis. The work has been interrupted, so it has been thought best to publish these results.

The gliadin used was prepared from a bakers' grade hard wheat flour by extracting with 60 per cent alcohol, filtering the extract until perfectly clear, concentrating and precipitating with absolute alcohol. The crude gliadin thus obtained was again dissolved and precipitated, digested repeatedly with ether, and finally dried over sulphuric acid. All alcohol and ether used had been carefully re-distilled. The preparation was soluble to a perfectly clear and almost colourless solution in dilute alcohol. Duplicate portions contained 17·42 per cent and 17·52 per cent of nitrogen, determined by the Gunning method, the digestion being continued for two hours after the mixture had become colourless. It was thoroughly mixed during and after the drying so that the nitrogen determinations might be consistent with the polarimetric observations. It is very probable that the proteid was not quite free from moisture ; and the specific rotations obtained have been corrected by multiplying by the factor 17/16/1747.

The gliadin was soluble in dilute methyl and propyl alcohols, and in glacial acetic acid, phenol, paracresol, and benzyl alcohol. A white precipitate, presumably gliadin, was produced when the phenol solution was treated with ether, acetone, or pyridine, and somewhat less readily when treated with benzene or chloroform. Pure methyl, ethyl, propyl, and amyl alcohols produced precipitates, the amount required being less the greater the molecular weight of the alcohol. No turbidity followed the addition of several volumes of aniline, phenylhydrazine, or nitrobenzene, but when gliadin was treated with these substances it did not seem to dissolve, and the clear filtrates showed practically no optical activity. It seemed somewhat soluble in benzaldehyde, but the sample of the latter used was not pure.

In order to ascertain whether the gliadin underwent decomposition on dissolving in phenol, about 7 grms. were taken, dissolved in about 100 cc. hot phenol, and the solution, after cooling, poured into about 500 cc. pure benzene. A heavy precipitate was produced, although the addition of a little of the supernatant liquid to benzene caused a further separation of solid material, showing that a considerable amount still remained dissolved. The liquid was decanted off, the precipitate washed repeatedly with benzene, drained with suction, and dried for three weeks over sulphuric acid *in vacuo*. It still retained a faint odour of phenol. Two portions were taken, dissolved in 70 per cent ethyl alcohol, and the solutions polarised. The latter were not absolutely clear, but were sufficiently clear to enable saccharimeter readings to be obtained without difficulty. Ten cc. were taken from the saccharimeter tube, and the nitrogen content determined. From this the specific rotation was calculated, assuming the gliadin to be equal to the nitrogen multiplied by 10000/1766. The following are the data :—

Saccharimeter reading, 40° C.		
100 mm. tube	− 4·53° V.	− 5·45° V.
Grm. of nitrogen in 100 cc.		
at 40° C.	0·3051	0·3678
$[\alpha]_D$ 40° C.	− 90·95	− 90·76

The specific rotation of the substance seems to have suffered but little change. It gave the biuret reaction and the red purple coloration with diluted sulphuric acid exactly as does pure gliadin. A solution of gliadin in phenol, giving a saccharimeter reading of − 19·7° V. (200 mm. tube), was sealed up in a glass bulb and maintained at a temperature of about 140° in an air-bath for three and one-half hours. It then gave a reading of − 18·4° V.

The solutions of gliadin in glacial acetic acid and in benzyl alcohol gave precipitates with ether exactly resembling gliadin in appearance, and which dissolved readily in dilute alcohol. These latter solutions gave the biuret reaction.

The specific rotations of the gliadin were obtained with a triple shadow saccharimeter, a jacketed tube being used for the solution. The following are the data :—

Solvent.	Grm. gliadin per cc. at 40°.	Saccharimeter reading in Ventzke degrees.	$[\alpha]_D$ 40. Degrees.
Methyl alcohol, 70 per cent	0·03644	− 19·81	− 95·3
,, 70 ,,	0·03366	− 18·42	− 96·0
Ethyl alcohol, 70 ,,	0·03085	− 16·21	− 92·1
,, 70 ,,	0·04499	− 23·55	− 91·8
,, 60 ,,	0·02264	− 12·52	− 96·9
,, 60 ,,	0·02388	− 13·13	− 96·4
,, 60 ,,	0·03126	− 17·25	− 96·7
,, 50 ,,	0·02895	− 16·29	− 98·6
,, 50 ,,	0·04914	− 27·55	− 98·3
Propyl alcohol, 60 ,,	0·02990	− 17·07	− 100·9
,, 60 ,,	0·03015	− 17·42	− 101·3
Phenol, 70 ,,	0·02035	− 14·25	− 122·7
,, 70 ,,	0·03340	− 23·56	− 123·6
Phenol, anhydrous	0·02824	− 21·31	− 132·2
,, ...	0·03018	− 22·73	− 132·0
,, ...	0·04288	− 32·07	− 131·1
Paracresol	0·02799	− 19·54	− 121·0
Glacial acetic acid	0·04267	− 19·69	− 80·9
,, ...	0·05014	− 22·48	− 78·6
Benzyl alcohol	0·02282	− 6·91	− 53·1
,, ...	0·03050	− 10·14	− 58·3

The methyl and propyl alcohols and the phenol used were the chemically pure grades from well-known manu-

facturers, and were fractionated before use. The acetic acid and cresol were chemically pure grade, but were not further purified. The benzyl alcohol was fractionated. It had a boiling-point of about 202° (uncorrected). The aromatic compounds were tested for optical activity.

The divergence in the results obtained with the benzyl alcohol is doubtless due to the decomposition of a part of the proteid by the heating necessary to bring it into solution. The sample giving the lower reading was purposely kept at a high temperature considerably longer than the other to see if the rotation would be markedly changed. Doubtless the other determinations are also affected with some error due to the same cause, although this was guarded against as far as was practicable.

The fact that gliadin is soluble in phenol would seem to render possible an approximate determination of its molecular weight by the freezing-point method. Since it is also soluble in boiling 70 per cent propyl alcohol, a determination by the boiling-point method might be made, since G. N. Lewis has shown (*Journ. Am. Chem. Soc.*, xxviii., 766) that Raoult's law regarding the elevation of the boiling-point can be applied to a binary solvent whose vapour has the same percentage composition as the liquid. The presence of traces of moisture would affect the results by the latter method much less, although gliadin is doubtless more or less altered by continued warming with any solvent containing water.

An attempt has been made to estimate the gliadin present in flour by digestion with phenol and polarisation of the filtered extract. The results obtained seem to indicate that a quite complete extraction of the gliadin is effected. It is possible, however, that more or less glutenin also dissolves in the phenol. The chief difficulty encountered is in the filtration of the mixtures.—*Journal of the American Chemical Society*, xxviii., No. 10.

THE DETERMINATION OF TUNGSTIC ACID IN WOLFRAMITE ORES AND CONCENTRATES.*

By HUGH F. WATTS, Boulder, Colorado.

On account of the tungsten production that has taken place in Colorado in the last few years, and which bids fair to be maintained, the following method of analysing its ores, while presenting nothing especially new, nevertheless may be found of interest:—

The samples of ores or concentrates, as they come to the assay office, are generally already prepared; if not, they should be made to pass a 100-mesh screen. A portion of the sample is then finely ground in an agate mortar, and, as much of the success of the determination depends on the fineness, it is necessary that this part of the operation be thoroughly done, as a few extra minutes spent in grinding may prevent the necessity of a second acid treatment.

One grm. of the finely ground material is then transferred to a four-ounce beaker and treated with 50 cc. concentrated hydrochloric acid and 15 cc. concentrated nitric acid, covered with a watch-glass and set on the hot plate. The degree of heat should be such that there is a gentle action of the acids on the mineral, but the solution should not actually boil. The decomposition takes about four hours and the solution should be occasionally well stirred up. At the end of this time the solution will have evaporated to about 10 cc. to 15 cc. and the walls of the beaker will be slightly covered with tungstic acid. It is not necessary to carry the evaporation to dryness, but if this is done, care must be taken not to overheat the residue, as otherwise the separated tungstic acid is rendered difficultly soluble in ammonia.

To the residue in the beaker add 50 cc. hot water and allow to settle for half-an-hour. Decant the clear solution through a good filter paper. The residue settles readily and can be decanted close. Wash the residue twice more by decantation, using each time 50 cc. hot water and 5 cc. hydrochloric acid, keeping as much of the residue in the beaker as possible. The use of hydrochloric acid in the wash water is to keep the tungstic acid from running through, which it has a tendency to do when washed with pure water.

The tungstic acid is now separated from the silica with dilute ammonia containing a small amount of ammonium chloride. It is convenient to have the ammonia in a small wash bottle (a four-ounce wash bottle is sufficient) containing 1 to 10 ammonia, to which is added 1 cc. strong hydrochloric acid. This small amount of ammonium chloride prevents silica from running through with the dissolved tungstic acid, and which it is disposed to do when washed with ammonia alone.

About 25 cc. of the ammonia solution are added to the beaker, washing off the cover glass and dissolving that which adheres to the sides. The tungstic acid readily goes into solution and is decanted through the filter to dissolve out all the acid retained. The residue of silica is now brought on the filter and washed thoroughly with the ammonia solution. The resulting silica should be white; if it shows any particles of undecomposed mineral, the decomposition must be repeated, using 25 cc. aqua regia, which will generally complete the work. One trial is all that is usually necessary if the ore has been finely ground and frequently stirred.

The ammoniacal solution is now evaporated, either in a weighed platinum or porcelain crucible. A 2½-inch porcelain is preferable on account of the facility with which the evaporation can be conducted. For my own use, for this evaporation, I employ an air bath of shallow construction, heated with Bunsens, and capable of holding four crucibles upon which the operation is carried on with a considerable saving of time over that required when a water bath was used.

When evaporation is complete, the crucible is heated over a Bunsen, gently, at first, to drive off ammonium salts, and finally at the highest heat of the burner, rotating the crucible to expose fresh surfaces to the heat. It is not desirable to use a blast for this purpose, as tungstic acid is slowly but steadily volatilised by an excessive heat.

The crucible is then cooled in a desiccator and weighed as tungstic acid. This is the form in which it is usually reported. If metallic tungsten is required the factor is 0·7931.

The acid, which adheres somewhat strongly to the crucible, can be removed by soaking over night in dilute ammonia. Then with the aid of a little silica, or, better still, powdered fluor-spar, and the finger, it can be readily and completely cleaned.

In the above scheme I have not found that the resulting tungstic acid contains more than inappreciable amounts of silica. If, however, the ammoniacal filtrate is in any way turbid, it is necessary to test for its presence. If the final evaporation has been made in platinum, this can be done by expelling the silica with hydrofluoric acid and re-weighing.—*Western Chemist and Metallurgist*, July, 1906.

Royal Institution.—On Tuesday next, January 15, at 3 o'clock, Professor Percy Gardner delivers the first of two lectures at the Royal Institution on "The Sculpture of Aegina in relation to Recent Discovery"; on Thursday, January 17, at 3 o'clock, Dr. W. N. Shaw begins a course of two lectures on "Recent Advances in the Exploration of the Atmosphere"; and on Saturday, January 19, at the same hour, Sir Alexander Mackenzie commences a course of two musically illustrated lectures on "Latest Phases of Music." The Discourse on January 18 will be delivered by Sir Andrew Noble, Bart., K.C.B., on "Fifty Years of Explosives," and on January 25 by Mr. C. Welch on "The Guildhall Library." Professor W. W. Watts being unable to deliver his two lectures on the "Building of Britain" and "Recent Light on Ancient Physiographies" on Thursdays, February 14 and 21, Mr. Alfred Harker will deliver two lectures on those dates on "The Minute Structures of Igneous Rocks, and their Significance."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting December 20th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

THE PRESIDENT announced that the following congratulatory telegram had been sent this day to Prof. Adolph Lieben (Honorary and Foreign Member of the Society), on the occasion of his seventieth birthday and the fiftieth anniversary of his Doctorate.

"Hearty congratulations to our Honorary and Foreign Member, Dr. Adolph Lieben, from the Chemical Society, London.—MELDOLA, President."

Messrs. W. R. S. Ladell, W. T. Lattey, and J. Mastin were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alfred Frederick Allen, B.Sc., 35, Parrett Road, Plumstead, S.E.; Henry Bassett, jun., B.Sc., Ph.D., 26, Belitha Villas, Barnsbury, N.; John Christie, B.A., Eton College, Windsor; Francis Davidson, Dover Place, Ashford, Kent; William Smith Denham, B.Sc., 2, Kelvinside Terrace North, Glasgow; George Fowles, 28, Weltje Road, Hammersmith, W.; William Godden, B.Sc., Station Road (East), Canterbury; Charles Pask Matthews, B.Sc., 6, Fortress Road, N.W.; Charles Schlienger, B.Sc., 273, Camden Road, N.; William George Sewell, B.Sc., 27, Park Road, Wandsworth Common, S.W.; Frederick George Shepheard, B.Sc., 9, Leinster Road, Rathmines, Co. Dublin.

Of the following papers, those marked * were read:—

*221. "*A New Laboratory Method for the Preparation of Hydrogen Sulphide.*" By FREDERICK ROBERT LEYLAND WILSON.

The common method for the preparation of hydrogen sulphide by the interaction of hydrochloric acid and ferrous sulphide is open to several objections, the most serious of which is the liability of the gas to contain the hydrides of arsenic and phosphorus, due to the contamination of the iron sulphide with phosphide and arsenide. The method here described ensures freedom from these impurities, as well as the absence of most of the unpleasant accompaniments of the ordinary process of preparation.

If a current of hydrogen sulphide is passed over an alkali hydroxide, for example, sodium or calcium hydroxides, a hydrosulphide is formed, heat being evolved and a change in colour from white to yellow taking place. If a current of carbon dioxide is now passed over the hydrosulphide, the compound is at once decomposed, a carbonate being formed and hydrogen sulphide set free.

In the case of calcium hydroxide, the yellow substance has the composition Ca(HS)(OH), and the action of carbon dioxide is given by the equation $Ca(HS)(OH)+CO_2=CaCO_3+H_2O+H_2S$.

A drying tower is filled either with granular soda-lime or an intimate mixture of calcium hydroxide and moist sawdust. A stream of hydrogen sulphide is passed into the tower until the contents are saturated with the gas, the course of the action being easily determined by the change in colour and by the movement of a heated zone upwards through the tower.

After the action has proceeded for some time the gas which escapes from the exit tube smells strongly of hydrogen phosphide and is inflammable, doubtless consisting of hydrogen mixed with all the other gaseous impurities evolved by the action of acid on the ferrous sulphide.

When the hydroxide has reacted with as much hydrogen sulphide as possible, a carbon dioxide generator is substituted for that supplying hydrogen sulphide, and the apparatus is ready to yield as slow or rapid a supply of the latter gas as may desired.

The supply of hydrogen sulphide ceases at once when the stream of carbon dioxide is cut off, and if the exit tube from the tower is closed, a partial vacuum will soon be produced owing to combination of the gases in the tower with unaltered hydroxide.

Owing to this absorption of the gas in the tower, it is only necessary to cut off the supply of carbon dioxide in order to prevent further escape of hydrogen sulphide.

The rate of supply of the gas may be nicely regulated by introducing a short length of capillary glass tubing between the carbon dioxide apparatus and the generating tower.

The danger of contamination of the hydrogen sulphide with carbon dioxide is very small, and may be entirely eliminated by making use of two towers. As soon as the first shows signs of exhaustion (indicated when calcium hydroxide is used, by the change in colour), it is replaced by the second tower; a new one is put in place of the latter, and the supply of gas taken from this.

DISCUSSION.

The PRESIDENT asked how the method compared with the known laboratory process of preparing hydrogen sulphide by heating sulphur with certain hydrocarbons such as solid paraffin.

Mr. WILSON stated that he had not compared the two methods.

*222. "*The Affinity Constants of Aminocarboxylic and Aminosulphonic Acids as Determined by the Aid of Methyl-orange.*" By VICTOR HERBERT VELEY.

The method of determining the affinity constants of acids by means of a very dilute methyl-orange solution and a tintometer described in a former paper (*Zeit. Physikal. Chem.*, 1906, lvii., 147), as applied to the carboxylic acids and certain chloro- and hydroxy-derivatives, has been extended to the aminocarboxylic and aminosulphonic acids. It is shown that the same general mathematical expressions hold good, namely, those of straight lines $y=kx$ or $y=kx-b$, or logarithmic curves $\log y=\log k+x\log a$.

Acids which show irregularities in the Ostwald electric conductivity expression $\phi(k)=a^2/(1-a)V.(a=\mu/\mu_\infty)$ likewise show similar irregularities in the methyl-orange method.

The aliphatic aminocarboxylic acids act as neutral substances, but their hydrochlorides as hydrochloric acid only, hydrolysis being nearly complete at the degree of dilution used.

The special cases of asparaginic acid, as possessing a higher affinity factor than succinic acid, and of cacodylic acid, as allied to amphoteric electrolytes, have been investigated.

The aminobenzoic acids show a distinct acid function, and the results obtained are in a similar arithmetical ratio to those deduced by Winkelblech (at a different degree of dilution) by the electric conductivity method.

The two aminobenzenesulphonic acids studied, namely, sulphanilic (1 : 4) and metanilic (1 : 3) acids are remarkable in that the latter conforms to the straight line, but the former to the logarithmic expression.

The introduction of a second sulphonic grouping diminishes rather than increases the acid function.

A study of the naphthylamine mono- and di-sulphonic acids (eighteen in number) affords examples of steric "furtherance" as regards the positions 2 and 7 relative to 1, and of steric hindrance as regards the position 8 relative to all other positions.

DISCUSSION.

Dr. CAIN suggested that, as the 1-naphthylamine-8-sulphonic acid exhibited the phenomenon of "steric hindrance" and the 1-naphthylamine-2-sulphonic acid that of "steric furtherance," it would be of interest to know the behaviour of the 1-naphthylamine-4-sulphonic acid, particularly as this underwent molecular change into the 1 : 2-acid by the action of heat.

Dr. HEWITT asked if there was any definite stage between the colour of methyl-orange in alkaline and in acid solution. He had himself compared the absorptions of methyl-orange and butter-yellow, and found that the

solutions of dimethylaminoazobenzene and sodium dimethylaminoazobenzenesulphonate, on the one hand, and the salts of butter-yellow and acidified solutions of methyl-orange on the other, gave practically identical absorption spectra. Any intermediate coloration between that of the free sulphonic acid and its sodium salt might be explained by partial neutralisation, and this opinion is confirmed by the fact that dimethylaminoazobenzenesulphonic acid in solution gives practically the same absorption as solutions of methyl-orange with an excess of mineral acid. The supposed free acid of methyl-orange would thus appear to be an internal salt.

The PRESIDENT asked whether special precautions had been taken to ensure the purity of the naphthylaminesulphonic acids used by the author, since the technical preparations supplied were professedly impure from the chemical point of view, and the difficulty of obtaining homogeneous products from mixtures of isomerides was often very great. With respect to the question of the proximity of position 8 as compared with position 2 relatively to position 1 in the naphthalene ring, he did not think that enough was known about the actual configuration of the atoms in the molecule to enable any dogmatic statement to be made.

Dr. VELEY, in reply, said that it would be unwise to express any dogmatic views as to the relative contiguity of substituent groupings in the naphthalene nucleus. As regards the position 4, a difficulty had arisen on account of the sparing solubility of the 1-naphthylamine-4-sulphonic acid. The acids had been purified previous to use by recrystallisation or otherwise. He felt some hesitation in discussing the actual composition of the yellow, orange-red, and red shades of methyl-orange, but it was clear that the last was the result of some more profound chemical change. In any case the hypothesis of migratory ions appeared to be too speculative.

*223. "*Contributions to the Study of the Calcium Phosphates. I. The Hydrates of the Calcium Hydrogen Orthophosphates.*" By HENRY BASSETT, jun.

Although numerous hydrates of dicalcium phosphate have been mentioned in the chemical literature, the author's experiments show that, in all probability, dicalcium phosphate can only form one hydrate, namely, the dihydrate.

The experiments also allow of some conclusions being drawn as to the position of certain of the quintuple points on the space model of the three-component system, $CaO—P_2O_5—H_2O$.

There are indications that the point at which the phases present are $CaHPO_4,2H_2O$, $CaHPO_4$; solid solutions (see the papers by Cameron and Seidell in *Journ. Am. Chem. Soc.*, 1905, xxvii., 1503, and Cameron and Bell, *Journ. Am. Chem. Soc.*, 1905, xxvii., 1513); liquid solution and vapour lies at about 80°; whilst the point at which the phases $CaH_4(PO_4)_2,H_2O$, $CaHPO_4,2H_2O$, $CaHPO_4$, liquid solution and vapour can co-exist lies at about 30°.

The monocalcium phosphate has also been studied, and it has been found possible to prepare the crystallised anhydrous salt. This compound can be obtained in long bright prisms by crystallisation at 160° of a solution of calcium carbonate in orthophosphoric acid if the ratio of P_2O_5 : CaO in the solution is sufficiently large. The best value for this ratio was found to be 4·6. If it is less than 3·0, then, even at 160°, the monocalcium phosphate monohydrate crystallises out.

*224. "*Contributions to the Study of the Calcium Phosphates. II. The Action of Ammonia Gas on the Calcium Hydrogen Orthophosphates.*" By HENRY BASSETT, jun.

It was found that under certain conditions when the acid calcium phosphates were treated with ammonia gas, absorption of the latter took place. The cause of this and the reactions occurring have been investigated with the following results:—

$CaHPO_4$ does not absorb ammonia either at the ordinary temperature or at 100°.

$CaHPO_4,2H_2O$ does not absorb ammonia at the ordinary temperature, but if heated in the gas to 100°, vigorous absorption takes place with formation of a mixture of tricalcium- and ammonium phosphates according to the equation—

$$3CaHPO_4,2H_2O + 2NH_3 = Ca_3(PO_4)_2 + (NH_4)_2HPO_4 + 6H_2O$$

When $CaHPO_4,2H_2O$ is heated, it would seem that at a temperature of about 80°, one of the quintuple points of the system $CaO—P_2O_5—H_2O$ is reached. At this temperature the dihydrate breaks up into a mixture of $CaHPO_4$, $Ca_3(PO_4)_2$ and solution, and it is in this solution that the above reaction with ammonia takes place.

$CaH_4(PO_4)_2$ absorbs ammonia very slowly at the ordinary temperature, but rapidly at 100° with formation of the compound $Ca(NH_4)_2H_2(PO_4)_2$. This compound is not stable in presence of water, which at once decomposes it into $CaHPO_4$ and $(NH_4)_2HPO_4$. This explains why, when $CaH_4(PO_4)_2H_2O$ reacts with ammonia gas, a mixture of $CaHPO_4$, $Ca_3(PO_4)_2$, and $(NH_4)_2HPO_4$ is formed.

The commencement of the ammonia absorption by the $CaH_4(PO_4)_2,H_2O$, is probably due to formation of the above calcium ammonium phosphate. This, however, liberates water of crystallisation, which at once forms some solution in which the reaction proceeds. Although this reaction first leads to the formation of $CaHPO_4$, this can further react with ammonia as long as any solution is present.

It is to this further reaction that the presence of $Ca_3(PO_4)_2$ in the final product is due.

DISCUSSION.

Dr. VELEY asked if the author had dried the ammonia gas, and if the phosphates experimented upon were quite free from traces of adherent moisture. It appeared that the subsequent solution in water of the products obtained introduced a very essential disturbing factor.

Dr. BASSETT, in reply, said that the ammonia used had been dried by passing over solid caustic soda and sodium wire, but, of course, such ammonia was not absolutely dry. The calcium phosphates used in the experiments were also as free from adherent moisture as was possible without extreme precautions. With regard to the examination of the reaction products by treatment with water, the author realised the dangers of the method and the possibility of reactions occurring during this treatment. The method had, however, been employed as being the only one which would enable one to distinguish between, for instance, a mixture of $Ca_3(PO_4)$ and $(NH_4)_2HPO_4$, and a compound $Ca(NH_4)PO_4$, and he considered that the difficulty caused by possible reactions during the extraction with water had been satisfactorily overcome in each particular case in the manner described in the paper.

*225. "*Relation between Chemical Constitution and Physiological Action in the Tropeines.*" By HOOPER ALBERT DICKINSON JOWETT and FRANK LEE PYMAN.

Reference was made to Ladenburg's generalisation, according to which a tropeine in order to possess mydriatic action must contain a benzene nucleus and a fatty hydroxyl in the side chain containing the carboxyl group, and also to a recent paper by Jowett and Hann (*Trans.*, 1906, lxxxix., 357), in which it was stated that terebyl- and phthalidecarboxyl-tropeines, which are lactones, and do not contain fatty hydroxyl groups, produce, nevertheless, marked dilatation of the pupil, and lose their physiological activity when converted into the corresponding hydroxy-acids.

The authors have prepared the *lactone* of *o-carboxyphenylglyceryltropeine*, expecting to find it very active physiologically, since it is not only a lactone, but also conforms to Ladenburg's generalisation, *isocoumarincarboxyltropeine*, which results on heating the above, and certain alkyl bromides of these tropeines and of homatropine.

The physiological examination showed that these tropeines are only slightly mydriatic, and that their

physiological activity is lost when they are converted into the corresponding hydroxy-acids. The authors conclude that Ladenburg's generalisation cannot be maintained, since it does not hold good either in the case of terebyltropeine or of the lactone of *o*-carboxyphenylglyceryl tropeine, but that the difference in activity between a lactone and its corresponding hydroxy-acid possesses important physiological significance.

(To be continued).

PHYSICAL SOCIETY.

December 14th, 1906.

Second Annual Exhibition of Electrical, Optical, and other Physical Apparatus.

Messrs. R. and J. Beck, Ltd.—Microscopic Resolution with Monochromatic Light. Wave-Length Spectroscope.

The Cambridge Scientific Instrument Co., Ltd.—Ballistic Balance. Optical Bench. Callendar and Griffiths's Wheatstone Bridge. Recording Mercury Thermometer. Chronograph for recording variations in speed. Chronograph for Morse Paper. New type of Oil-Bath Oscillograph. Burton's Anti-Vibration Stand.

Messrs. Casella and Co.—6-inch Transit Theodolite. Alpine Transit Theodolite. Whipple-Casella Universal Sunshine Recorder. Anderson's Patent Slide-Rule. Recording Pressure-Guage. Portable Dip Circle. Casella's Patent Self-Recording Anemometer.

Messrs. Crompton and Co.—Portable Testing Set. Steam Car Pyrometer. Electrical Pyrometer for Boiler Installation.

Messrs. Elliott Bros.—Simple Astatic Galvanometer. Glass Cylinder Galvonometer. Brass Case Galvanometer. Moving-coil Galvanometer. Five-dial Wheatstone Bridge. Standard Resistances. Perforator with Desk and Stand. Portable Fault-Localising Bridge. "Century" Mains Test Set. Subdivided Condenser. Set of Die Castings. Simplex Indicator. Harrison Universal Photometer. Key Repeater Boatd.

Messrs. Evereet, Edgecumbe, and Co.—Iron-clad Wattmeter for General Purposes. "Universal" Moving-iron Ammeters and Voltmeters. Adjustable Resistances for Laboratory Purposes. Combined Standard Ammeter and Voltmeter. Frequency Indicator, of the Resonance Pattern. Direct-reading Resistance Bridge.

Messrs. Evershed and Vignoles.—Apparatus for measuring resistance.

Messrs. Gambrell Bros.—Standard Inductance. Galvalnometer with strained suspension. Galvanometer with levelling screws. Carey-Foster Bridge. Universal Shunt. Series Resistance Box, Reversing Switches. Testing Set.

Messrs. A. Hilger, Ltd.—Spectrophotometer, with Attachment for using also as a Spectro-polarimeter. Lummer Parallel Plate Spectroscope.

Messrs. Nalder Bros. and Thompson, Ltd.—Portable Standard Testing Sets. Portable Instruments, Ammeters and Voltmeters. Portable Insulation Testing Set: The "Ohmer."

Messrs. Newton and Co.—Goold's Vortex Plates. Goold's Vortex Plates, showing Dispersion figures.

Mr. R. W. Paul.—Duddell-Mather Standard Wattmeters. Duddell-Mather Gauze Resistances. Reflecting and Pivoted Electrostatic Voltmeters. Reflecting Galvanometer, with New Scale Stand and Nernst Lamp. Shunt-boxes. Campbell Standard Bifilar Galvanometer. Resistance Standards. Portable Galvanometers. Paul-Harris Test Wire. Portable Testing Sets, Milli-voltmeters, and Micro-ammeters. Nernst-Paul Lamps and Lanterns. Universal Pyrometers, and a small Electric Muffle Furnace.

Messrs. James Pitkin and Co.—Holden D'Arsonval Galvanometers. Pitkin-White Pivoted Moving-coil Galvanometers. Electrical Pyrometers. Resistance Boxes, Standard Cells, Scale Stands. Measuring Instruments.

Messrs. Reynolds and Branson, Ltd.—Universal Science Lantern. "Rystos" Electric Lantern with Capstan Arc Lamps. "R. and B." Electric Arc Lamp. R. and B. "Phœnix" Focus-keeping Arc Lamp. R. and B. Patent "Capstan" Arc Lamp. "Rystos" Photo-Micrographic Apparatus. "Rystos" Lantern Microscope. Barr and Stroud's Lantern Slide Apparatus. "Rystos" Reflecting Galvanometer. "Rystos" Electric Dark Room Lamps. Geometrical Models.

Messrs. Ross, Ltd.—"Standard" Petrological Microscope (No. 2). "Standard" Metallurgical Microscope (No. 2). Combination Lantern.

Messrs. J. Swift and Son.—Petrological Microscope.

Dr. W. M. Watts.—Binocular Diffraction Spectroscope.

Messrs. Alexander Wright and Co.—Simmance and Abady Patent Combustion Recorder.

Messrs. Carl Zeiss.—Abbe Refractometer with Heating Arrangement. Butter Refractometer. Measuring Microscope for Metal Testing. Microscope for Measuring Capillary Tubes. Dipping Refractometer.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 26, December 24, 1906.

A Colloidal Compound of Thorium with Uranium.—Béla Szilard.—On precipitating a hydrate of thorium with ammonia, washing well with warm water, and then mixing the precipitate with a solution of uranium nitrate, the mixture undergoes no change. On raising the temperature, the hydrate loses its white colour, and becomes reddish, the solution having formed a colloidal mixture with the precipitate. Various means were tried for the investigation of this phenomenon, the most successful being the preparation of the body by another method. A solution of $UO_2(NO_3)_2$ (about 2 per cent) was prepared, boiled, and mixed with the freshly prepared and well washed hydrate of thorium, until only a red liquid remained (the hydrate of thorium itself is dissolved in the clear liquid). This red colour is not intensified by increasing the relative amount of uranium, but it is intensified by increasing the quantity of thorium, which seems to corroborate the hypothesis that the body is a compound. The colloidal solution of thorium hydrate prepared with thorium nitrate has no reaction similar to that with uranium nitrate. The chloride, UO_2Cl_2, may be substituted for the nitrate of uranium with the same effect, but in this case the colour is yellowish red; with the acetate and sulphate of uranium, the reaction proceeds much more slowly. Analysis gives the following percentage composition of the body:—Th, 72—74; U, 4—5·5; H_2O, 12—13; O, 10—11, per cent. Zirconium and some other bodies possess, equally with thorium, this property of forming colloidal compounds with salts of uranium.

The Absolute Atomic Weight of Dysprosium.—Gustave D. Hinrichs.—In his recently published results of his determinations of the atomic weight of dysprosium (*Comptes Rendus*, 1906, cxliii., p. 598), G. Urbain has carefully pointed out the degree of purity of the products employed by him. This circumstance gives, with regard to the question of *absolute atomic* weights, a greater importance to his new work than to his work on the atomic weight of terbium reviewed previously (*Comptes Rendus*, 1906, cxlii., p. 1196). M. Urbain gives two series of determinations; the first referring to his treatment of nitrates, and giving only a "first approximation"; the second to his treatment of ethylsulphates, in which the earths were in a state of greater purity. In his calcula-

tions, M. Urbain adopted H = 1·007 and S = 32·06, which values have been shown to be erroneous since 1892. Hence the values calculated do not accord with the degree of purity attained. The author therefore applies to the experimental results of M. Urbain the method of absolute calculation already worked out in the case of his determinations of the atomic weight of terbium. M. Urbain weighed the crystallised sulphate, and the residue left by this salt after calcination. For Dy = 162·5 the atomic weight of the crystallised sulphate, $Dy_2(SO_4)_3 + 8H_2O$, is 757, and the atomic weight of the oxide, Dy_2O_3, is 373 exactly; for the absolute values H = 1 and S = 32 exactly. The atomic ratio is $\frac{\text{oxide}}{\text{sulphate}} = \frac{373}{757} = 0{\cdot}49273$; the analysis of M. Urbain give the following analytical excesses:—

	Fractions.	Experimental results (G. Urbain). Sulphate (grms.)	Oxide (grms.)	Calculation of experimental results (G. D. Hinrichs). Analytical ratio.	Analytical excess.
			Series I.		
35	I. ..	1·6965	0·8359	0·49269	−4
	II. ..	2·0926	1·0301	226	−47
38	I. ..	1·8415	0·9069	248	−25
	II. ..	1·5519	0·7649	288	+15
41	I. ..	2·4955	1·2296	273	0
	II. ..	1·8130	0·8927	239	−34
			Series II.		
9	I. ..	1·8817	0·9271	0·49269	−4
	II. ..	1·1164	0·5500	266	−7
8	I. ..	1·7308	0·8528	272	−1
	II. ..	2·6038	1·2820	236	−37
7	I. ..	1·6942	0·8346	262	−11
	II. ..	2·1776	1·0726	256	−17

The analytical excesses are in perfect agreement with the indications of purity given by the eminent analyst. For the first series (earths arising from the nitrates) the variations of the two determinations made for each fraction are:

No. 35	From	−4 to −47	about 43
„ 38	„	−25 „ +15	„ 40
„ 41	„	0 „ −34	„ 34
	Mean		39

For the second series (earths arising from the ethyl sulphates):—

No. 9	From	−4 to −7	about 3
„ 8	„	−1 „ −37	„ 36
„ 7	„	−11 „ −17	„ 6
	Mean		15

Therefore the variation of the second series is less than half that of the first. Further, the extreme values in the first are −47 and +15, corresponding to a total variation of 62; while in the second series the extreme values are −1 and −37, corresponding to a total variation of 36. It is remarkable that the fraction giving the most accurate values, *i.e.*, those showing the least analytical excesses, is the fraction No. 9, which M. Urbain considers the purest of all. This agreement between experiment and calculation cannot be regarded as fortuitous, and it must therefore be concluded that the absolute atomic weight of dysprosium is 162·5 exactly.

The Definite Compounds formed by Chromium and Boron.—Binet du Jassonneix.—The reduction of chromium oxide by boron in the electric furnace in crucibles of magnesium yields fusions containing from 5 to 17 per cent of boron combined with chromium; a systematic study of their properties has been made in order to classify and isolate the definite compounds which they might contain. Specimens containing percentages of boron varying from 4·9 to 11·6 were examined; microscopic examination showed that these bodies consisted of two different substances, one acting as a kind of cement to the other, which increased in proportion to the percentage of boron; the specimen with 11·6 per cent boron is almost homogeneous. The results after several analyses, on the lines indicated in a previous note, were as follows:—

	I.	II.	III.	IV.	V.	VI.	Theoretical for Cr_3B_2.
Percentage boron ..	11·9	12·1	12·2	12·2	12·4	12·6	12·3
Percentage Cr . ..	87·3	87·4	87·7	87·5	—	87·2	87·7

Thus the existence of a definite compound of formula Cr_3B_2 is confirmed. Another series of experiments, conducted on specimens containing from 16 to 17 per cent boron, which were found to consist almost entirely of one only of the two definite media, led to the discovery of the definite compound CrB:—

	I.	II.	III.	IV.	Theoretical for CrB
Percentage B..	17·3	17·2	16·9	17·1	17·4
„ Cr..	82·5	82·5	82·8	82·4	82·6

Hence the fused products of chromium and boron contain two definite compounds, Cr_3B_2 and CrB, dissolved respectively in a medium less rich in boron.

Anhydrous Protoxides of the Alkali Metals.—E. Rengade.—The author has prepared protoxides of rubidium, potassium, and sodium, never before obtained in a pure state, by applying to these metals the method by which he had already obtained the protoxide of cæsium. Thus the partial oxidation of the alkali metals, followed by distillation *in vacuo* of the excess of the metal, produces in a pure state the anhydrous protoxides, Cs_2O, Rb_2O, K_2O, and Na_2O; but these do not crystallise readily as in the case of cæsium protoxide.

NOTES AND QUERIES.

, Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Filter Press.—We shall shortly be requiring to purchase a filter press, and should be greatly obliged if any reader would give us information as to the best firms to whom to apply for this apparatus.—C. R. L.

MEETINGS FOR THE WEEK.

TUESDAY, 15th.—Royal Institution, 3. "The Sculpture of Aegina in Relation to Recent Discovery," by Prof. Percy Gardner, Litt.D., &c.

—— Society of Arts, 4.30. "The Progress of the Uganda Protectorate," by George Wilson, C.B.

—— Faraday Society, 8. "Application of the Electron Theory to Electrolysis," by E. E. Fournier D'Albe.

WEDNESDAY, 16th.—Society of Arts, 8. Adjourned Discussion on Mr. J. W. Gordon's paper on "Patent Law Reform."

—— Microscopical, 8. Annual Address by the President, "The Flowering Plants of the Mesozoic Age in the Light of Recent Discoveries." Exhibition of Mounted Specimens of Freshwater Polyzoa, by Mr. Rousselet.

THURSDAY, 17th.—Royal Institution, 3. "Recent Advances in the Exploration of the Atmosphere," by W. N. Shaw, M.A., &c.

—— Chemical, 8.30. "Relation between Absorption Spectra and Optical Rotatory Power—Part I., Effect of Unsaturation and Stereoisomerism," by A. W. Stewart. "Organic Derivatives of Silicon.—Part II., Synthesis of *dl*-Ethyl-propyl-benzyl-silicol, its Sulphonation, and the Resolution of the Sulphonic Derivatives into Optically Active Compounds," by F. S. Kipping. "Association of Phenols in the Liquid Condition," by J. F. Hewitt and T. F. Winmill. "A New Mercuric Oxychloride," by J. T. Hewitt. "Aromatic Selenonium Bases," by S. Smiles and T. P. Hilditch. "Relation of Colour and Fluorescence to Constitution," by A. G. Green. "Constitution of Silver Nitrite" (a Correction), by E. Divers. "Preparation of Chromyl Chloride," by F. D. Law and F. M. Perkin. "Tetraketopiperazine," by A. F. de Mouipied and A. Rule.

FRIDAY, 18th.—Royal Institution, 9. "Fifty Years of Explosives," by Sir Andrew Noble, Bart., K.C.B., &c.

SATURDAY, 19th.—Royal Institution, 3. "Latest Phases of Music" (with Musical Illustrations), by Sir Alexander C. Mackenzie, Mus. Doc., &c.

A I.C., aged 22, with two years' practical experience, desires Post in Analytical Laboratory.—Address, "A 22," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

Analytical Chemist and Bacteriologist, B.Sc. (Lond.), A.I.C., nine years' practical experience of every description of Analytical work, desires a Post in Public Analyst's Laboratory. Highest references.—Address, "Analyst," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

Advertiser, having six years' experience as Chemist and Assistant Manager in large Works, desires Post Well up in all branches of Inorganic Analysis. Low salary if prospect of rapid advancement. Disengaged Feb. 1st.—Address, W. F., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

Analytical Chemist, B.Sc. (Manchester), with knowledge of Bacteriology, Biological Chemistry, Water and Sewage Analysis, &c., desires Appointment in Sewage Disposal or Chemical Works, or Analysts' Laboratory. Six years' experience; four years at Owens College, Manchester; French and German.—Address, "Alpha," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

Analytical Chemist, eight years' experience in large Steel works and four years Chief Assistant in Public Laboratory, desires Position as Head Chemist or Chief Assistant in Works or other Laboratory. Best references.—Address, Clark, 49, St. Ann's Road, Rotherham.

Junior Assistant wanted in Analytical Laboratory. One with knowledge of Brewing Analysis preferred State experience, &c.—Apply, 20, Kilvert's Buildings, Witby Grove, Manchester.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2460.

CALCIUM AS AN ABSORBENT OF GASES FOR THE PRODUCTION OF HIGH VACUA AND SPECTROSCOPIC RESEARCH.*

By FREDERICK SODDY, M.A., Lecturer in Physical Chemistry in the University of Glasgow.

(Continued from p. 15).

V. *Behaviour of Barium and Strontium.*

Tested under the same conditions, barium and strontium show very analogous behaviour to calcium. The specimen of barium employed had been preserved under oil, and was in the form of a granular powder. It had been prepared from the amalgam and still contained mercury. It was given a preliminary heating *in vacuo* to remove oil and some of the mercury. It commenced to absorb gases without appreciable volatilisation at a temperature notably below that required in the case of calcium. A non-conducting vacuum was usually not obtained before the metal had been allowed to cool. In the work with both barium and strontium the hydrocarbon spectrum, reminiscent of the argon gases, was very frequently observed, and was probably due to traces of the oil in which the metals had been preserved. This spectrum usually appeared when the metal was hot, and disappeared on lowering the temperature, the vacuum becoming non-conducting. Coal-gas was admitted to the heated barium to a pressure of 2 to 3 mm., and was rapidly absorbed, and a non-conducting vacuum obtained without difficulty. Air introduced to about 7 mm. pressure was rapidly absorbed, except for argon, exactly as with calcium.

Barium *can* be heated to its absorbing temperature in a hard glass tube by a Bunsen burner, but the tube collapses and cracks on cooling. Under similar circumstances calcium requires a blowpipe to induce volatilisation and absorption, and the tube is completely melted and flows round the calcium in the process.

Experiments with strontium were less complete on account of the difficulty of obtaining the real metal, and on account of the small quantities that had to be used. The first sample bought as strontium proved to be potassium amalgam simply, without sufficient strontium to give a precipitate with sulphuric acid. The metal, when it was obtained, proved to be similar in properties to barium and calcium. On account of the cost only a decigramme at a time could be used, and it is very probable that its behaviour, as observed, was partly due to presence of alkali metals, oil, and mercury, and that electrolytic strontium in compact form, free from these contaminations, would exhibit a behaviour even more nearly allied to calcium. So far it has not been possible to procure this. Absorption with the sample employed seemed to start at a slightly higher temperature than with calcium, and at a high temperature some volatilisation of the metal appeared to occur. This was due probably to a trace of alkali metal. It showed to a very marked extent the phenomenon of not giving a good vacuum until it had been cooled down, and of showing hydrocarbon spectra very strongly, but this behaviour might not be shown by an oil-free specimen. It seemed hardly worth while to pursue experiments with a metal at once so costly and so impure, when a commercial process has been patented for producing the metal on a scale similar to that of calcium. But the experiments proved that, like barium and calcium, it can absorb coal-gas and air, and give a non-conducting vacuum without difficulty.

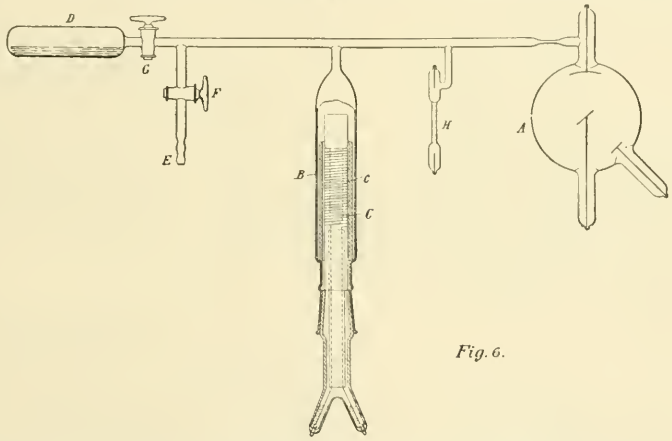


Fig. 6.

VI. *Production of High Vacua by Means of Calcium.*

From what has been said it will be seen that the apparatus described affords a ready means of obtaining a high vacuum by the use of calcium as an absorbent. Arndt, in the paper referred to, suggested its use in the production of high vacua, on account of the energetic action of the vapour on the residual air. A little consideration, however, shows that since argon is not absorbed by the reagent, air must be as rigorously as possible excluded. As is well known, the real difficulty in the production of high vacua depends not so much on the removal of all the original air, which is comparatively easily and quickly accomplished even with a pump, but on the effective removal of the gases which are condensed on the glass walls of the vessel being exhausted, and which tend to re-condense in the pump when driven out of the vessel, and to introduce a kind of steady vapour pressure until they have all been removed. The value of calcium

* Read before the Royal Society, November 15th, 1906

as a means of producing the highest vacua depends on its power to absorb almost instantly the gases condensed on the glass walls as soon as the latter are expelled by heating. It is, as stated, necessary to replace all the air in the apparatus before the absorption with calcium takes place, or the residual argon will prevent the vacuum obtained from being really good. The importance of this is increased by the fact that articles for exhaustion have usually to be provided with a very constricted orifice, so that they can be sealed safely after the vacuum has been obtained. As a consequence, any argon accumulating in the absorp-

Fig 7.

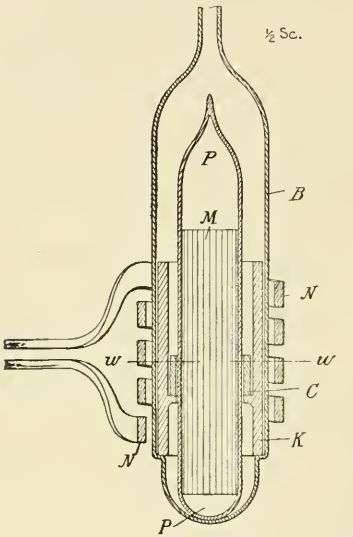
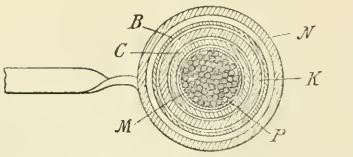


Fig. 8.



tion chamber dams back the flow of absorbable gas from the vessel being exhausted, and enormously increases the time required, as the contents of the vessels have to diffuse and mix through the constricted orifice, and this process may require some minutes. Hence, in this method of high vacua production, the customary precautions must be taken against the leakage of air, if really high vacua, as distinguished from the apparently high vacua later to be considered, are desired.

If a Fleuss pump in good order is available, and new glass apparatus which has not before been exhausted is being dealt with, it suffices to continue the pumping while the apparatus in question is heated in the usual way to expel condensed gases, and so utilise the latter to replace the residual air remaining in the apparatus. Or, if a new charge of calcium, not previously heated in a vacuum, is employed, the same displacement of the air can be readily effected by the gases given out by the calcium before it attains its absorption temperature. In both cases the gases consist chiefly of carbon and hydrogen compounds, and, being free from argon, serve well for the displacement of the remaining air. In other cases, or where more certainty is desirable, the complete replacement of the air may be effected by the use of a side tube containing a mixture of potassium chlorate and manganese dioxide, which evolves oxygen on warming. One or two small quantities of oxygen are admitted during the pumping, and the connection with the pump closed or sealed off before the calcium is brought into action. Fig. 6 shows, in diagram, an apparatus suited for the purpose of exhausting an X-ray bulb. C is the calcium heated by the platinum wire *c* within the glass vessel B. A is an X-ray tube, and D is a tube containing the oxygen mixture. The Fleuss pump is connected with E, and the spectrum tube H is a convenience both for judging of the degree of vacuum and the character of the residual gas.

With this method, as in all methods of vacua production, the degree of rarefaction attained is the balance between the rate of absorption or removal of the gas present, and the rate of supply of fresh gas from leaks or from condensed films, or from substances such as lubricating grease or mercury which have a vapour pressure. Since the rate of absorption is extremely rapid good results can be obtained even under poor conditions. Conditions have to be very bad indeed for any difficulty to be experienced in the production of a so-called "X-ray" or "non-conducting" vacuum. But it will be shown in the sequel that these electric discharge phenomena may be produced in vacua which could not be described as high in any other sense. With proper care the very highest vacua may be obtained by the use of calcium, as is proved by the experiment quoted in Section IV, of filling the apparatus with mercury and compressing the gaseous contents several hundred times. Personally, in crucial experiments, I should use it preferably to any other, and in the research on the positive charge carried by the α-particle it was the final court of appeal, by which results obtained by other methods were always re-tried (*Nature*, August 2, 1906, p. 316).

VII. *An Induction Method of Electrically Heated Calcium in Glass Vessels.*

Calcium is an excellent conductor of electricity, being the fifth best if wires of equal length and diameter (Ag, Cu, Au, Al, Ca), and the third best if wires of equal length and weight (Na, Li, Ca, Mg, K, Al) are compared. Its volatility, relatively low melting-point, and low resistance are all against the possibility of heating calcium to its absorbing temperature by conducting a current through it. But in the form of fairly massive discs or rings calcium may be heated to its melting-point by induction through the glass walls of the containing vessel by means of alternating circuits outside the vessel. For instance, if a bundle of iron wires, similar to the core of an induction coil, is put through a ring turned out of a bar of calcium, and the whole placed in an exhausted glass tube, the walls of which are protected from fusion by a porcelain shield-tube in the manner before described, and a bobbin of insulated wire traversed by an alternating current of high periodicity be slipped over the glass tube, the calcium may be readily heated to its absorption and volatilisation temperature. The arrangement is simply a step-down transformer, in which the calcium ring acts as the single short-circuited winding of the secondary, and being of low resistance a fraction of a volt induced in it by the magnetic flux suffices to cause the passage of a heavy current, probably of the order of a kilo-ampère, which heats it to the required high temperature. Fig. 7 shows one arrangement for this purpose.

Fig. 8 is a transverse section on the line *ww*. The iron core M is enclosed in a thin tube of Jena glass P, which is exhausted and sealed. This tube effects the double purpose of protecting the iron from excessive heat and retaining gases given off from the iron, but can be dispensed with. C is the calcium ring, K is the porcelain shield-tube, B is the outer glass containing tube, N is the external circuit through which the inducing current is passed. As the heat given out from the calcium is considerable and apt to injure insulating material, it is convenient to employ, instead of a bobbin of insulated wire of many turns, a few turns of stout, bare, copper bar or tube, and to obtain the inducing current from the secondary of a step-down transformer not shown in the drawing. Since the magnetic flux, and therefore the inducing voltage in C, varies as the square of the diameter of the core, while the resistance of C varies as the diameter, it follows that the larger the diameter of cross-section of the apparatus the easier it is to obtain the desired result. But the induced voltage depends also on the periodicity of the inducing current, so that the latter must be the higher the smaller the apparatus employed. The dynamo employed was specially constructed for the purpose, and gave with variation of speed a periodicity from 200 to 400 cycles per second. The drawing shows the apparatus to the scale of 6 inches to the foot.

Another form of apparatus is shown in Fig. 9, to the scale of 3 inches to the foot. It differs from the last mainly in that the magnetic circuit, composed of the iron strips or wires M_2 M M M_2, is closed, but for the two air gaps where the glass walls of the containing vessel penetrate it. The use of the step-down transformer is unnecessary, because the inducing bobbins, represented diagrammatically by the circuit N N N N, are far enough removed from the source of heat not to be damaged. The part within the glass containing vessel is shown to twice the scale (6 inches to the foot) in Fig. 10. Fig. 11 is a section of the same. Figs. 12 and 13 are transverse sections in vertical and horizontal planes respectively. C is a disc of calcium bored with a central hole through which passes the bundle of iron wires M M. P_2 P_2 are two porcelain crucible lids bored with central holes. Instead of the disc of calcium shown, a disc one-third the thickness between two similar discs of copper may be employed if it is required to increase the conductivity. Since in these induction methods of heating the heat is developed in the reagent itself, the latter is hotter than its surroundings, which is a great advantage, as far less screening of the glass walls suffices. The temperature of the metal can be very accurately judged by the eye, and must be kept below the melting-point. A moderate red-heat just above the cherry-red stage is necessary for absorption of gases and volatilisation to occur.

Fig. 9.

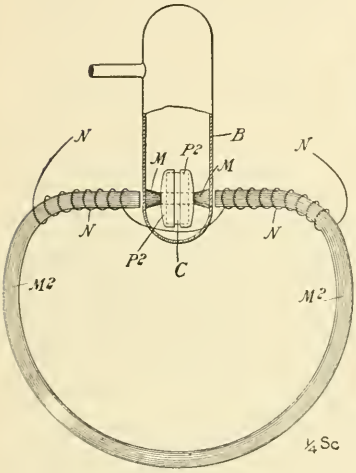


Fig. 10.

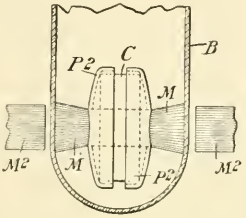


Fig. 12

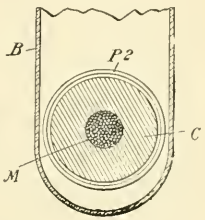


Fig. 11.

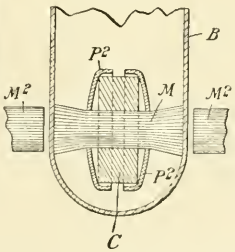
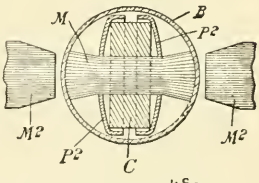


Fig. 13.



For experimental work where cost is not the primary consideration, and where frequent dismantling of the apparatus is rendered necessary, the resistance furnace method of heating is to be preferred. But for prolonged work in which the object is simply to obtain a high vacuum, the induction method offers great advantages.

VIII. *Some Practical Considerations in the use of Calcium as an Absorbent for the Production of High Vacua.*

There is no doubt that a low initial pressure, not exceeding a few millimetres of mercury, is as essential a condition in causing calcium to combine with gases as a high temperature. As Arndt showed, there is a slight initial absorption below the volatilisation temperature, and this is of great practical importance. For rapid and continuous absorption volatilisation is essential. But in a case where the initial pressure is above that at which volatilisation occurs, the slight initial action is often sufficient to lower the pressure to the extent necessary for the formation of vapour. When this has once taken place subsequent absorption is much facilitated, for the film of volatilised metal continues, even in the cold, to absorb, although more

slowly than the vapour itself. Hence, once volatilisation has taken place there is present a tendency to re-establish the condition for further vaporisation. When, however, a mixture with an unabsorbable constituent, for example, air, is being absorbed, the accumulation of this constituent hinders the volatilisation and further absorption by the calcium. Another factor operating in the same direction is the increased loss of heat by convection currents in the presence of a gas, tending to lower the temperature of the reagent and furnace, and to lower the resistance of the latter. In the usual case, where this resistance is small compared to the external resistance in the circuit, the fraction of the electrical energy dissipated within the furnace is also lowered, and so the temperature falls from a double cause. If water vapour is present the action becomes extremely marked on account of the great conductivity of this vapour to heat. The current necessary to raise the temperature in this case may be so great, that unless promptly reduced when absorption commences the heating circuit is apt to be destroyed.

Under proper conditions of working the calcium should never be melted, although it may be volatilised completely and re-deposited on the cooler part of the tube as a compact tube or ring difficult to remove by mechanical means. Used porcelain tubes should never be exposed to the air or treated with water or dilute acids, as they readily crack under this treatment. Immersion in concentrated hydrochloric acid usually serves to dissolve the volatilised metal without cracking the tube, but with the liberation of the spontaneously inflammable silicon hydride. If the calcium is melted in the tube the latter usually cracks on cooling, so that for many reasons suitable iron tubes would be better than porcelain. The narrow margin of temperature, 70° C. according to Arndt, between the volatilisation and melting-point need, however, never be exceeded when experience has been gained and suitable metal is employed. The presence of hydride in the metal acts so prejudicially, largely because the dissociation tension of hydrogen lessens the volatilisation and reduces still further this narrow margin, so that the melting-point is the more likely to be overstepped. These conclusions as to the conditions under which calcium should be employed as an absorbent have been arrived at after over a year's continuous use of the method.

The following experiment on the effect of vapour of grease and of a very constricted orifice between the vessel being exhausted and the absorption chamber is instructive. An X-ray bulb was connected to the calcium absorption apparatus provided with a ground-joint. The latter was lubricated by the well-known mixture of rubber, paraffin-wax, and vaseline, employed by Sir W. Ramsay. A spectrum-tube was provided and the apparatus exhausted by the Fleuss pump, and the connection with the latter sealed off. The calcium was brought into action and a vacuum corresponding to an alternative spark-gap of 15 cm. obtained in the X-ray tube. It was then left over night in connection with the furnace, so that the vapour from the grease of the ground-joint could exert its full effect. In the morning the vacuum was so low that there was no trace of green fluorescence in the tube. The calcium was heated and allowed to cool. In forty minutes the 15 cm. alternative spark-gap was again attained.

Then, hour by hour, the vacuum slowly deteriorated till the alternative spark-gap was *nil* and the green fluorescence disappeared. This process of heating the calcium and leaving till the vacuum went right down was repeated day by day for a week. It was noticed that it always took forty minutes after heating the calcium before the 15 cm. spark-gap was regained, and this period represented, as numerous experiments with the same tube show, the time taken by the gases to flow out of the X-ray bulb through the constricted orifice when a practically perfect vacuum existed on the other side. It happened that the constriction was unusually and unnecessarily narrow, such as an amateur not realising the importance of it would make, but the necessity of this constriction, where the tube is ultimately to be sealed off, imposes a natural limit on the time taken for the exhaustion, however rapid a method of absorption is employed. In this experiment the spectrum in the Plücker tube, when the vacuum was low, was due to hydrocarbons, and nitrogen was never seen. That there was no appreciable leak of air was also shown by the fact that even at the end of a week no lines of argon could be seen. This shows that the deterioration of the vacuum was simply due to vapour being slowly given off from the grease used for lubrication. A properly constructed ground-joint is wonderfully air-tight. I may mention that in 1904 I constructed one of Strutt's so-called radium clocks with a ground-joint similar to those employed in the furnaces. The period of the clock is the same now as when constructed, and it has worked continuously without re-exhaustion, proving conclusively that no trace of air has leaked through the ground-joint. Hence, in the calcium method, where the vapours of lubricants are absorbed with rapidity, as many taps, ground-joints, and similar conveniences as desired may be employed without harm, provided they are well lubricated and never get heated, and that the apparatus being exhausted is sealed off as soon as the high vacuum is attained.

(To be continued).

THE APPLICATION OF THE ELECTRON THEORY TO ELECTROLYSIS.*

By E. E. FOURNIER-D'ALBE.

THE electron theory of electricity and magnetism may be fitly described as an extension of the ionic theory of electrochemistry to solids, gases, and a vacuum, inasmuch as it postulates material carriers of all electric charges, and reduces electric phenomena to the configuration and motion of these carriers. The application of the electron theory to electrolysis means, therefore, no revolutionary change in electrochemical conceptions, but simply an attempt to bring our extended knowledge of the properties of the elementary carriers of electricity to bear upon well-known phenomena, and thus to gain a clearer insight into the actual mechanism of electrolytic conduction and dissociation.

One of the most valuable achievements of the electron theory is the complete harmonisation of the processes of metallic and electrolytic conduction. Both processes depend upon the existence of minute charged bodies capable of threading their way through a mass of other bodies which are either uncharged or less mobile. If a body contains no such charged bodies—ions in the wider tense—or if its ions are fixed in position, it is incapable of conveying an electric current of any description. A current consists in the displacement of ions. The conductivity of a body is accurately and precisely defined by the number of ions it contains in unit volume and by their average mobility; this mobility, in its usual acceptation, excluding any measurable free path. The definition and physical interpretation of conductivity is thus the same in liquids and solids.

It is only when we consider the individual carriers themselves that a fundamental difference appears between metallic and electrolytic conduction. Compare a cm.-cube of copper with a cm.-cube of dilute hydrochloric acid, each of them conveying a current of one ampère. The copper conveys its current almost solely by its free electrons, some 400 million in number, which possess a mobility some 100 million times greater than that of a hydrogen ion. The hydrochloric acid conveys the current by means of its hydrogen and chlorine ions, which, in a millinormal solution, amount to about 2 million. Since the current is the same in each case, the electrons in the copper must move

* Abstract of a Paper read before the Faraday Society, January 15, 1907.

some two hundred times more slowly than in the electrolyte. But this is not usually the case, for in a copper wire 1 mm. in diameter conveying one ampère the speed of the electrons is of the order of 1 cm. per second. The greatly superior mobility of the free electrons brings it about that a much lower voltage is required to maintain an ampère in a copper conductor than in a liquid conductor of the same dimensions.

Whence this difference between solids and liquids? At first sight it seems strange that free electrons should be observable in a vacuum and traceable in a metal, but that there should be none in a liquid. The elucidation of this question would be of fundamental importance for the theory of electrolysis, and would constitute a valuable contribution from the general theory to the special field to which, as a matter of fact, it owes its origin.

It cannot be said that this question is anywhere near a complete solution. But since the whole range of electromagnetic phenomena has become unified under the sway of the electron theory, much additional material has become available upon which to base our judgment.

The existence of free electrons in metals is made possible by the close packing of their atoms, which brings about a frequent exchange of electrons between one atom and another. During the short period occupied by its change of allegiance—a period amounting to something like 1/5000th of its average time of attachment to a metallic atom—the electron is free to fall along the potential gradient, and thus to constitute an electric current. When the metal expands by heat, this process of exchange naturally becomes rarer, and the metallic resistance increases. The positive atoms and neutral atoms are so tightly packed that they contribute nothing perceptible to the conductivity.

In an insulating solid or liquid the electrons are effectively bound up with atoms or molecular groups, and these are arranged in some structure, usually crystalline in the case of solids, which precludes the formation of mobile charged groups and the liberation of electrons.

In an electrolyte, on the other hand, such charged groups are formed, and they are sufficiently mobile to follow the E.M.F. That free electrons are not produced is capable of a simple explanation. Two copper atoms have equal attonitions for an electron, but atoms of, say, hydrogen and chlorine have not. Hydrogen loses one of its electrons more easily than chlorine, and when the two atoms of a molecule of hydrochloric acid separate, the chlorine takes one of the normal hydrogen electrons away with it. The hydrogen atom thus remains positively charged, and the chlorine atom negatively. The two ions so produced act as condensation nuclei, like any other small charged particles. The study of electric condensation nuclei will, I believe, shed a flood of light on electrolytic problems. The fundamental researches of C. T. R. Wilson have proved that in vapours, at all events, ions act as condensation nuclei, and that negative ions are slightly more effective than positive ions (*Phil. Trans.*, 1897, clxxxix., p. 265). Of this phenomenon J. J. Thomson has furnished a simple explanation ("Conduction of Electricity through Gases," 2nd ed., p. 179).

When a charged drop evaporates its electric charge remains, and its potential increases as its diameter diminishes. More energy is therefore required to evaporate a charged drop than an uncharged drop. Condensation on the drop involves an expenditure of available electric energy, and thus condensation is facilitated. This fact has an important bearing on the theory of electrolysis. It explains the low mobility of the ions, the drop of potential at the electrodes, and the liberation of uncharged products at the latter. The different mobilities of the ions can, I think, only be attributed to their different degrees of normal hydration. That hydroxyl should have a mobility over four times that of lithium points to the lithium atom as a particularly efficient condensation nucleus when deprived of one electron. It moves so slowly through the water under the influence of the potential gradient, because it has to drag a number of water molecules (probably not more than half a dozen) along with it. The number must be the same for each ion at a given temperature, but cannot be very large, to judge from the actual mobility (347×10^{-6}) compared with that of the electron in copper (about 5×10^{4}).

When these hydrated ions reach the electrodes the E.M.F. tends to drive them into the metal of the electrodes. But the atoms of the latter are so closely packed, as a rule, that no other atoms can force themselves between them. There arises a deadlock, which is only released when electrons are able to pass from the solution into the metal, or *vice versâ*. The mobility of electrons, though comparatively great inside a metal, is very small at its surface, where the close packing of the metallic atoms loses its effect. But when the E.M.F. exceeds a certain minimum an electron may pass, say, into a hydrogen ion, and neutralise its positive charge. The immediate consequence will be that the hydrogen loses its condensing power. The link between it and the water molecules is broken, and the hydrogen is liberated as an uncharged gas. The converse process goes on at the anode. The chlorine atom passes its superfluous electron into the anode, thereby becoming neutral and free from its aqueous encumbrance.

In the further theoretical investigation of electrolytic action on the basis of the electron theory the study of mobilities will have to play a prominent part. Bredig's laws of mobility are of special interest in this connection. We require a quantitative determination of the hydration of the ions. This determination should not be very difficult, since a number of data, such as heats of solution, melting and boiling-points, are ready to hand. It should be possible to determine the diameter and bulk of the ions, and their shape from stereochemical considerations. The fact, noted by Bredig, that the strongly electropositive and electronegative metals have a high mobility points to a superior facility of reaction.

A high mobility implies a low degree of hydration of the ion. This low degree of hydration enables such ions, when of opposite signs, to combine more freely and rapidly than is the case in ions having a larger bulk. The heats of reaction, the heats of ionisation, and the electro-affinities or electrode potentials of the majority of elements are fairly well known, and afford valuable data for determining the sizes of the ions. We already know that isomeric and metameric ions have the same mobility; that the mobility of an ion of a given sign is the smaller the greater the number of atoms it contains; and that the effect of any change in the constitution of an ion is the greater the smaller the number of atoms contained in the ion.

These facts leave the road clear for a determination of the actual constitution of a single ion on kinetic principles. When an iron contains 50 or 60 atoms it appears to have a minimum mobility which is not perceptibly diminished by a further addition of atoms. Such an ion must have a diameter of about a micromillimetre, and therefore comes within the range of Szigmondy's ultramicroscope. There is, therefore, a possibility that the motion of such heavy ions may be studied by actual observation, and that they may be watched as they cover a distance of 1 cm. in an hour and a half under the influence of a potential gradient of 1 volt per cm. It then becomes a comparatively simple calculation to find the diameter of such an approximately spherical ion moving through a viscous liquid, or, in the last resort, threading its way among molecules of perhaps half its diameter. Such calculations have been made in connection with metallic conduction, and have led to the conclusion that the carriers of the current in a wire are almost solely the free electrons.

A difficulty is presented by the circumstance that ions of the higher valencies exhibit mobilities which are neither "independent" nor constant for different concentrations (see Kohlrausch and Grüneisen, *Sitzungsber. Berlin Akad.*, xl., July 28, 1904). The extraordinarily high mobility of lead is not easily harmonised with our notions of the physical constitution of the ions. But it is interesting to

note that the influence of hydration increases with the valency and the concentration, which is what we should expect.

The future development of electrolytic theory will lie, I think, in the direction of statistical analysis on kinetic principles. Such analyses have yielded most suggestive results in gas discharges, more especially the electric arc, in the vacuum tube, the Zeeman phenomenon, and, quite recently, in metallic conduction. Thomson's famous "counting experiment" must be followed up. He produced ions in a moist gas, and watched them as they settled down under the influence of gravity. We must follow their motions along the potential gradient in a liquid, and follow the fate of the electrons they convey through the liquid into one electrode, and back into the liquid through the other. The complete determination of the energy absorbed or emitted at the various stages of this transmission means the complete mastery of the problems of electrolysis.

THE NITRATION OF ANILINE AND CERTAIN OF ITS DERIVATIVES.

By J. BISHOP TINGLE, Ph.D., F.C.S., and F. C. BLANCK.

It is well known that aniline cannot be directly nitrated; under any of the ordinary conditions in which such action might be expected to take place, nitric acid converts aniline into a resinous, tarry, or charred mass. This behaviour is usually accounted for by stating that the nitric acid attacks the amino group more readily than the benzene nucleus (*vide*, for example, Lassar-Cohn's "Application of some General Organic Reactions," translated by J. Bishop Tingle, p. 3, *et seq.*). A little thought will show that such a statement, although it *may* be true, is really devoid of any experimental foundation, and that certain rather serious objections could be urged against it. For instance, it has been suggested by some chemists that substitution in the nucleus is really preceded by the substitution in the side chain, and subsequent re-arrangement. Further, the amino group is even more sensitive towards nitrous acid than towards nitric acid, as is shown by the fact that, in general, nitrites of the aromatic amines cannot be prepared, whereas the nitrates are usually stable; moreover, in carrying out the diazo reaction, some tarry matter is always formed, and unless considerable care is taken to adjust the conditions of the experiment specially for each individual amine, this tar is apt to be the chief, or even the only tangible product of the reaction.

Guided by these considerations, we decided to re-investigate the direct nitration of aniline, and to begin a systematic survey of the influence, on nitration, of the substitution in aniline of one or both of the hydrogen atoms of the amino group. Coupled with this, however, is the further question of the influence exercised on the substitution by admixture of the nitric acid with other acids. These points are illustrated by the fact that dimethylaniline yields the paranitro derivative when nitrated in the presence of acetic acid (*Ber.*, x., 761), whereas the meta compound is formed if sulphuric and nitric acids be used (*Ber.*, xix., 198). A number of cases are on record where mixtures of nitric and acetic acids *or* nitric and sulphuric acids have been employed to nitrate some compound, but this is the only example which we have been able to find in the literature of nitration experiments having been made on a given aniline derivative with each of these mixtures of acids. The influence of the substituting group is shown by the fact that formanilide, for example, yields the paranitro derivative by direct nitration (*Am. Chem. Journ.*, viii., 346), whereas, under the same conditions, acetanilide gives rise to a mixture of ortho and paranitro compounds (*Jahresb.*, 1875, p. 344; *Am. Chem. Journ.*, xi., 320).

The investigation just outlined will, naturally, extend over a considerable time, and we wish to reserve the field by the publication of this paper, which, although it is of a preliminary nature, contains results that we think may prove to be of some general interest.

Nitration of Aniline.—Our experiments in this connection being based upon the hypothesis that nitrous acid might probably be the active agent in producing the decomposition of the aniline, we took every precaution in our power to exclude this substance, and to remove it if it were formed. Accordingly, the nitric acid which was used was freed from dissolved oxides by means of a current of dry air, and, as far as possible, oxidation during the experiment was avoided by employing nitric acid of 99 per cent concentration and freshly distilled aniline. We carried out the experiments in platinum vessels, placed in a freezing mixture, so as to keep the temperature as low as possible, and took care that the reagents were gradually mixed and thoroughly stirred; moreover, we operated in the presence of urea, in the hope that any nitrous acid which might be produced by the possible reduction of some of the nitric acid would be instantly decomposed by this reagent. In the later experiments we employed aniline nitrate in place of aniline, so as to eliminate the heat of formation of this salt. In every experiment, however, it was found to be impossible to keep the temperature sufficiently low, and, as soon as it rose, tarry or carbonaceous products were formed. The result was identical whether the acid was added to the aniline or *vice versâ*.

These experiments were therefore discontinued and another series undertaken in order to determine at what concentration of nitric acid the formation of aniline nitrate ceases and nitration—or charring—begins. The results demonstrated that any strength of acid could be used up to at least 75·33 per cent HNO_3, provided, in the case of the more concentrated acids, above 50 per cent, that the mixture was cooled and excess of acid was avoided. Acids of 50·71 to 75·33 per cent always gave, with aniline, a pink-coloured solid, which was stable at 0°; the colour was at once discharged by the addition of a little water or of a few drops of aniline. Slight excess of acid increased or restored the colour, as the case might be, but if this additional acid was of sufficient concentration, then, sooner or later, depending on this concentration and on the temperature, the pink colour darkened, finally becoming black, and the whole mass gradually charred, sometimes becoming incandescent. We have been unable to find any previous record of these phenomena.

With acid above 75·33 per cent HNO_3, charring took place rather quickly, although the aniline was in considerable excess. We believe, however, that this was due to the impossibility of preventing local superheating; *i.e.*, to the action of the concentrated acid, at a relatively high temperature, on aniline nitrate. Be this as it may, it is certain that with acids containing up to 75·33 per cent HNO_3, any charring which may be brought about is due to an attack on aniline nitrate and not to one on free aniline. We emphasise this rather obvious fact in order to contrast it with the behaviour of aniline towards a mixture of nitric and sulphuric acids, in which the latter is in considerable excess. In these circumstances, as is well known, nitration proceeds smoothly, because, as it is usually expressed, the sulphuric acid "protects" the amino group. Surely, however, the amino group is equally well "protected" in the nitrate, $C_6H_5NH_3NO_3$, as in the sulphate, $C_6H_5NH_3SO_4H$, and the excess of concentrated sulphuric acid which is present must abstract so much water from the nitric acid as to make it of a higher concentration than 75·33 per cent HNO_3. The only very obvious difference in the conditions of the two experiments, so far as we can see, is in that which governs the temperature. In the experiment with sulphuric acid all the materials are in solution, and the "heat of nitration," as it may be termed, is instantaneously absorbed and diffused throughout the large volume of comparatively indifferent sulphuric acid, whereas in our experiments with aniline nitrate and nitric acid we had to rely on the relatively slow, inefficient, and clumsy mechanical means of stirring

and external cooling to neutralise this heat. We hope, later, to recur to this point, when more experimental data have been accumulated.

Nitration of Aniline Substituted in the Amino Group.—A considerable amount of scattered work, which will be cited in due course, has been done on the nitration of compounds of the types C_6H_5NHR, C_6H_5NRR' and $C_6H_5N{:}R''$, and in some of these experiments the nitric acid was mixed with sulphuric or acetic acids. This portion of our investigation has been carried out with the following reagents:—1. Nitric acid, sp. gr. = 1·46, containing 80 per cent HNO_3 (Remsen and Graham, *Am. Chem. Journ.*, xi., 320). 2. Nitric acid, sp. gr. = 1·46, with glacial acetic acid, usually in the proportion 1·25 mols. of nitric acid to 4 mols. of acetic acid, or 1·25 mols. of nitric acid to 8 mols. of acetic acid. 3. Nitric acid, sp. gr. = 1·46, and anhydrous oxalic acid, in the proportion 1·25 mols. of nitric acid to 4 mols. of oxalic acid. 4. Nitric acid, sp. gr. = 1·46, and trichloracetic acid, in the proportion 1·25 mols. of nitric acid to 4 mols. of trichloracetic acid, 5. Nitric acid, sp. gr. = 1·46, and concentrated sulphuric acid, sp. gr. = 1·83, containing about 92 per cent H_2SO_4, in the proportion of 1·25 mols. nitric acid to 4 mols. of sulphuric acid. The dissociation constants of these admixed acids are as follows:—Acetic acid, K = 0·0018; oxalic acid, K = 10·00; trichloracetic acid, K = 121·00; sulphuric acid, K = 130·0, approximately, by calculation. It will be observed that we have selected, for admixture with the nitric acid, acids of widely differing strength. Acetic is a typical "weak" acid; trichloracetic is, practically, the strongest organic acid which is known, and certainly the strongest which is available for use in any quantity. Oxalic acid was selected partly because it is dibasic, but chiefly because of its intermediate position between the other two. The use of sulphuric acid was dictated by the fact that it is the only "strong" inorganic acid suited for the purpose in view. It will be noticed that, in so far as "strength" is concerned, sulphuric and trichloracetic acids are in the same class (*cf.* Kastle, *Am. Chem. Journ.*, 1905, xxxiii., 52), and should therefore permit of a conclusion being drawn as to the influence, if any, of the mono or dibasicity of the admixed acid, and of its organic or inorganic composition, *i.e.*, as to the possible specific influence of a carboxyl group.

As far as possible, we desired to avoid the formation of di- or polynitro derivatives; consequently, our experiments were usually carried out at room temperature; in cases where there was a considerable evolution of heat on mixing the substances, cooling with ice-water was resorted to. Sometimes the mixtures were surrounded by crushed ice during the whole time of an experiment, and occasionally gentle warming was requisite to promote a reaction.

Formanilide.—This substance yields paranitroformanilide by direct nitration (*Am. Chem. Journ.*, viii., 346). In the presence of sulphuric acid we have obtained the *meta derivative*.

Acetanilide.—This compound, by direct nitration, gives a mixture of ortho and para derivatives (*Jahres.*, 1875, p. 344; *Am. Chem. Journ.*, xi., 320). In the presence of acetic acid no nitration took place under the conditions of our experiments. With oxalic acid we obtained *paranitroacetanilide* in good yield. The same result was produced by the use of trichloracetic acid, which was ground up with the acetanilide, and the mixture added to the nitric acid. Sulphuric acid yielded *metanitroacetanilide*. This last result differs from the experience of Nolting and Collin, (*Ber.*, xvii., 261), who, however, operated in a freezing mixture of ice and salt, and, nitrating in the presence of both acetic and sulphuric acids, obtained the para and ortho derivatives.

Benzoylanilide.—A mixture of ortho, meta, and paranitro derivatives is formed by the direct nitration of this compound (*Liebig's Ann. Chem.*, ccviii., 292). Operating in the presence of sulphuric acid we have only found the *para compound*.

By the use of acetic acid we have obtained the *meta isomer*, practically without admixture.

Methylaniline.—Our experiments with this substance, in the presence of acetic acid, failed to yield any positive result. Sulphuric acid causes the production of the metanitro derivative (*Centralbl.*, 1901, i., p. 105.

Ethylaniline.—This body behaved, with acetic acid, like the methyl compound. In the presence of sulphuric acid meta and para derivatives are formed (*Ber.*, xix., 546).

Dimethylaniline.—For the sake of completeness we include this substance, although we have no results of our own to communicate at present. Acetic acid is stated to produce the paranitro derivative (*Ber.*, x., 761), whereas sulphuric acid gives rise to the meta compound (*Ber.*, xix., 198).

Diethylaniline.—In our experiments with this substance, in the presence of acetic acid, nitration failed to take place. Sulphuric acid has been found to produce chiefly the meta derivative, together with some para compound (*Ber.*, xix., 199).

We think that our results justify the statement that *the position assumed by the entrant nitro group is definitely influenced both by the acid present with the nitric and also by the N-substituents.*

We hope to give full details of our experiments later, when the work on the subject, which is now in progress in the Johns Hopkins laboratory, is more nearly complete. —*American Chemical Journal*, xxxvi., No. 6.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting December 20th, 1906.

Prof. R. Meldola, F.R.S., President, in the Chair.

(Concluded from p. 22).

226. "*Some Derivatives of Salicylic Acid.*" By Hooper Albert Dickinson and Frank Lee Pyman.

In the course of the production of some derivatives of salicylic acid which might possibly find application in medicine, *cinnamoylsalicylic acid*, its *methyl* and *ethyl esters*, and *quinine salt*, and also 3 : 5-*dichloroacetylsalicylic acid* were prepared and characterised.

Cinnamoylsalicylic acid, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CH{:}CHPh$. Ten grms. of salicylic acid and 12 grms. of cinnamoyl chloride were heated together on a water-bath during three and a-half hours. The end of the reaction was indicated by the mixture becoming quite solid. After two re-crystallisations from benzene, *cinnamoylsalicylic acid* was obtained in a pure state, and in quantity amounting to 48 per cent of the theoretical yield; it crystallises from benzene in needles melting at 155°; is very readily soluble in alcohol or ether, sparingly so in chloroform or benzene, and almost insoluble in water:—

0·2409 gave 0·6316 CO_2 and 0·0981 H_2O. C = 71·5, H = 4·5.

$C_{16}H_{12}O_4$ requires C = 71·6, H = 4·5 per cent.

The *quinine salt*, $C_{16}H_{12}O_4,C_{20}H_{24}O_2N_2$, crystallises from alcohol in needles which melt at 169°. It is almost insoluble in water or cold alcohol:—

0·2151 gave 0·5729 CO_2 and 0·1208 H_2O. C = 72·5, H = 6·2.

$C_{16}H_{12}O_4,C_{20}H_{24}O_2N_2$ requires C = 72·9, H = 6·1 per cent.

The *methyl ester* was prepared by the condensation of molecular quantities of cinnamoyl chloride and methyl salicylate by means of anhydrous potassium carbonate. The product was purified by first treating with hot water, dissolving in chloroform, drying this solution, and mixing the oil which resulted after the removal of the solvent with light petroleum. On then re-crystallising from alcohol, the pure ester was obtained in large tabular crystals melting at 71° and in an amount equal to 63 per cent of the theoretical yield:—

0·2320 gave 0·6144 CO_2 and 0·1049 H_2O. C = 72·2, H = 5·0.
$C_{17}H_{14}O_4$ requires C = 72·3, H = 5·0 per cent.

The *ethyl ester*, obtained in an analogous manner, crystallises from alcohol in fine needles melting at 66—67°:

0·2433 gave 0·6476 CO_2 and 0·1182 H_2O. C = 72·6, H = 5·4.
$C_{18}H_{16}O_4$ requires C = 72·9, H = 5·4 per cent.

3 : 5-*Dichloroacetylsalicylic acid*, $C_9H_6O_4Cl_2$. This substance was prepared by the acetylation of 3 : 5-dichlorosalicylic acid with acetic anhydride and sodium acetate. It crystallises from benzene in needles melting at 159°:—

0·3350 gave 0·5328 CO_2 and 0·0732 H_2O. C = 43·4, H = 2·4.
0·2060 „ 0·2358 AgCl. Cl = 28·3.
$C_9H_6O_4Cl_2$ requires C = 43·4, H = 2·4, Cl = 28·5 per cent.

227. "*The Addition of Bromine to Cinnamic Acid and its Esters.*" (Preliminary Notice). By John Joseph Sudborough and John Thomas.

The appearance of a communication from W. Herz and Bruno Mylius in the last number of the *Berichte* (1906, xxxix., 3816) on the velocity of the addition of bromine to cinnamic acid induces us to give a preliminary account of experiments made by us on the same subject. All our experiments were conducted in pure dry carbon tetrachloride at 15°. The bromine used was the commercial product dried with sulphuric acid. We find that the velocity varies enormously according as the reaction proceeds in the dark or in daylight.

The following numbers calculated by means of the equation for a bimolecular reaction, when molecular proportions of bromine and of cinnamic acid, namely, some 0·0333 mol. per litre, are used, show this clearly.

Cinnamic Acid.—K (in dark). Series 1 : 0·0054, 0·0044, 0·0066, 0·010, 0·013. Series 2 : 0·0072, 0·0074, 0·0066, 0·012.

K (in diffused daylight). Series 1 : 0·28, 0·33, 0·36, 0·33. Series 2 : 0·41, 0·37, 0·31, 0·34, 0·30, 0·31.

Similar results have been obtained when the methyl and ethyl esters are used.

Methyl Ester.—K (in dark). Series 1 : 0·0058, 0·0060, 0·0058, 0·0089, 0·0089, 0·0081. Series 2 : 0·0047, 0·0047, 0·0039, 0·0062, 0·0089, 0·0071. Series 3 : 0·0049, 0·0091, 0·0071, 0·0079, 0·0095.

Ethyl Ester.—K (in dark). Series 1 : 0·0085, 0·0074, 0·0077, 0·010, 0·011, 0·012. Series 2 : 0·0071, 0·0074, 0·0053, 0·0076, 0·012, 0·010. Series 3 : 0·0044, 0·0048, 0·0050, 0·0050, 0·0049.

(In diffused daylight) 0·29, 0·25, 0·25, 0·30. (In sunlight) 1·85, 1·70, 1·60, 1·29, 1·62, 1·49.

The velocity constant with crotonic acid is smaller than with cinnamic acid.

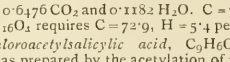
Crotonic acid (in dark) K = 0·00096, 0·00094, 0·00069, 0·00101.

All the experiments were made in glass-stoppered bottles, not in sealed tubes; those conducted in the dark were in amber-brown coloured, the others in colourless bottles.

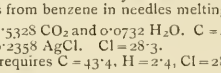
We wish to extend the work in the direction of studying the effect of the introduction of various substituents into the crotonic and cinnamic acid molecules.

228. "*The Optical and Magneto-optical Influence of Ethenoid Linkings Attached to Contiguous Carbon Atoms.*" By Julius Wilhelm Brühl.

It has been found by Sir W. H Perkin that limonene and dipentene (I)., and $\Delta^{3:8(9)}$-*p*-menthadiene (II.)



I.



II.

exhibit a remarkable difference in magnetic rotation, the values of II. being much higher than those of I. The author showed that this is due to the presence of two double linkings in the position —C:C·C:C— in the molecule of $\Delta^{3:8(9)}$-*p*-menthadiene.

229. "*A Difficulty in Theory of Valency of W. Barlow and W. J. Pope.*" By David Leonard Chapman.

In a recent number of the *Transactions* (1906, p. 1675), W. Barlow and W. J. Pope claim to have demonstrated that the doctrine of valency follows as a necessary consequence of certain simple assumptions as to the nature and mode of packing of the atoms. The consequences of the theory have not as yet been fully worked out; for the present, therefore, it will be best to restrict any remarks to an examination of the premisses. An analysis of these has disclosed a difficulty which appears to be of importance and to necessitate some modification of the fundamental assumptions.

In the paper in question the following is laid down as the first geometrical property of spheres:—"If in a close-packed assemblage of spheres, single spheres or groups of two or more, selected homogeneously, are replaced homogeneously by other groups of spheres in such a way that the resulting assemblage is close-packed without resorting to re-marshalling, the replacing group is of practically the same relative magnitude as the group replaced, and possesses the same fundamental valency" (*Trans.*, p. 1724).

A second geometrical property is stated thus:—"If a sphere of volume m (an atom of valency m) is replaced by one of volume $m+n$ (valency $m+n$) one or more additional spheres (atoms) having the total volume n (valency n) must be simultaneously inserted in order that the close-packing may be re-established without re-marshalling" (*Trans.*, p. 1729).

It is declared that from these propositions the law of the equivalence of elements and compound radicles can be immediately deduced, and the fact that an element of fundamental valency m can function as one of valency $m+2n$ is said to receive by means of them a rational explanation.

It will now be shown that different results can be deduced from the propositions in question. Consider a close-packed homogeneous assemblage, the similar parts of which are built up of spheres of the relative volumes—

$$2n_1, 2n_2 \ldots\ldots 2n_n, 2;$$

when n_1, n_2, &c., are whole numbers.

Replace the sphere of volume 2 by two spheres each of volume 1. According to the geometrical property of spheres formulated first above, this can be done without re-marshalling being involved. Now replace one of the spheres of volume 1 by two spheres of respective volumes 2 and 1, and finally replace the two spheres of unit volume by a single sphere of volume 2. The original system has now been converted into one composed of spheres of volumes represented by the numbers—

$$2n_1, 2n_2 \ldots\ldots 2n_n, 2,2$$

without re-marshalling, and by three substitutions in two of which the first geometrical property and in one of which the second geometrical property have been assumed to hold.

Now we are not concerned with the absolute dimensions of the system, and therefore the initial group of spheres can be regarded as consisting of spheres of the volumes—

$$n_1, n_2 \ldots\ldots n_n, 1,$$

and the final group of spheres can be regarded as consisting of spheres of the volumes—

$$n_1, n_2 \ldots\ldots n_n, 1, 1,$$

the marshalling being the same in both cases.

Therefore two spheres of volume 1 can function as one sphere of volume 1. By similar reasoning it can be shown that a sphere of volume 2 can function as a sphere of volume 1, and in general that a sphere of any size can replace any other without any resort to re-marshalling being necessary.

From the foregoing argument it would appear that the two propositions quoted above cannot be used alone (in their present unqualified form at any rate) to demonstrate

that valency is a simple volume relation. A formal statement, from the authors, of the restrictions to be put upon their use would be of value.

230. "*On the more Exact Determination of the Densities of Crystals.*" By the Earl of Berkeley.

A conical pyknometer with thermometer stopper and graduated side-tube is used, and instead of filling to a mark, the author relies on the evaporation of the liquid (round the neck) to bring the level in the capillary side-tube within the graduations.

The liquid used is carbon tetrachloride, and care is taken that the temperature of the balance case varies but little while the pyknometer is being weighed.

The air adhering to the crystals is expelled by causing a current of carbon tetrachloride vapour to pass over them when in an exhausted vessel, and the pyknometer is filled while still in this vacuous space. A desiccator was described whereby hygroscopic salts may be dried in a current of hot air, and the pyknometer filled in a vacuum. Results for the density of quartz, barytes, and potassium carbonate were given. The maximum difference between any two observations out of eleven on quartz, and out of nine on barytes, is 0·02 per cent. The experiments on potassium carbonate do not agree so closely.

231. "*A Relation between the Volumes of the Atoms of certain Compounds at the Melting-points and their Valencies. Interpretation by Means of the Barlow-Pope Theory.*" By Gervaise Le Bas.

The molecular volumes of complex paraffins and alcohols can be calculated very exactly by means of the formula :—

$$\text{M. V. of } C_nH_{2n+2} = (6n+2)S = 6nS = 2S,$$

where S is a constant which has an average value of 2·070, and is called the unit-stere. It is a measure of the volume of hydrogen. Carbon, in accordance with its valency, is equal to 4S. The value of S is also obtained by dividing the difference for CH_2 by 6. The numbers obtained in this way confirm the previous values.

Certain alcohols up to heptadecyl carbinol, $C_{18}H_{37}OH$, have also been studied, and their volumes are calculated by means of the expression—

$$\text{M. V. of } C_nH_{2n+1}OH = (6n+4)S = 6nS + 4S,$$

S having the same value as in the former series. Oxygen is thus found to have a volume equal to 2S in accordance with its valency-number.

These results were discussed in the light of the Barlow-Pope theory (*Trans.*, 1906, lxxxix., 1675).

232. "*The Action of Acid Chlorides on Thioureas.*" By Augustus Edward Dixon and John Hawthorne.

In former communications it has been shown that alkyl and aryl chlorocarbonates unite with thiourea, forming the hydrochlorides of basic derivatives, or pseudo-thioureas, $NH_2{\cdot}C(NH){\cdot}S{\cdot}CO_2{\cdot}R$; it is now established that Claus' compound of thiourea and acetyl chloride (*Ber.*, 1875, viii., 42) is similarly constituted.

Acetyl chloride unites spontaneously with monosubstituted aryl-thioureas, yielding compounds of the form $ArNH{\cdot}C(NH){\cdot}S{\cdot}COMe,HCl$; from these the corresponding picrates may be prepared. On withdrawing the combined hydrochloric acid by calcium carbonate or sodium ethoxide, the odour of thioacetic acid becomes perceptible; hence the base is probably liberated and then hydrolysed to a slight extent. Nevertheless, the product left on evaporation of the solution is not the free base, but an isomeride, the acetyl group having migrated from the sulphur to a nitrogen atom, so as to yield $AcArN{\cdot}CS{\cdot}NH_2$. The latter compound is known to change readily, by migration of its acyl group, into another isomeride, namely, the symmetrical $AcNH{\cdot}CS{\cdot}NHAr$; it appears, therefore, that by this series of transfers the acetyl group may be passed, in a given thiourea molecule, from point to point, until it has occupied, in succession, every position of attachment which a substituting group can assume. If the hydrogen chloride is eliminated by heat alone, the symmetrical or *ab*-thiocarbamide is produced; in like manner, Claus' compound yields acetylthiourea.

Benzoyl chloride behaves with thiourea and its aryl monosubstitution derivatives similarly to acetyl chloride; both chlorides unite with *ab*-aryl disubstituted thiocarbamides to form molecular additive products, the constitution of which has not yet been determined.

Disubstituted carbamic chlorides unite with thiourea, forming haloid salts; the corresponding nitrates and picrates are sparingly soluble in water.

Organic acid chlorides do not appear to combine with thioureas, which already contain an acidic group.

233. "*3-Hydroxyphthalic and 3-Methoxyphthalic Acids and their Derivatives.*" By William Henry Bentley, Rona Robinson, and Charles Weizmann.

An account was given of the preparation of 3-methoxyphthalic acid by the oxidation of 1 : 5-methoxynaphthol with alkaline permanganate, and of 3-hydroxyphthalic acid by fusion of 3-methoxyphthalic acid with caustic potash. A number of derivatives of each acid were described.

234. "*4-Hydroxyphthalic and 4-Methoxyphthalic Acids.*" By William Henry Bentley and Charles Weizmann.

The preparation of pure 4-hydroxyphthalic acid (m. p. 205°) from sulphophthalic acid by fusion with caustic potash was described, together with a number of derivatives of this acid.

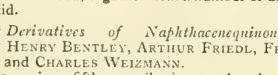
235. "*Derivatives of Naphthacenequinone.*" By William Henry Bentley, Arthur Friedl, Frederick Thomas, and Charles Weizmann.

This paper is a fifth contribution to the chemistry of naphthacenequinone (compare Diechler and Weizmann, Orchardson and Weizmann, *Ber.*, 1903, xxxvi., 547, 719, 2326; *Trans.*, 1906, lxxxix., 116), and contains a description of the preparation and properties of a large number of new hydroxy- and aminohydroxy-derivatives of this series.

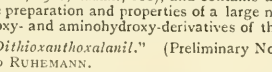
236. "*Dithioxanthoxalanil.*" (Preliminary Note). By Siegfried Ruhemann.

Thioacetanilide reacts with ethyl oxalate in the presence of sodium ethoxide to yield a compound similar to those which are formed from acetanilide and its homologues (Ruhemann, *Trans.*, 1906, lxxxix., 1236; *Proc.*, 1906, xxii., 284).

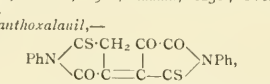
Dithioxanthoxalanil,—



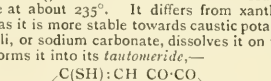
crystallises from glacial acetic acid in brown needles which decompose at about 235°. It differs from xanthoxalanil inasmuch as it is more stable towards caustic potash. The dilute alkali, or sodium carbonate, dissolves it on warming and transforms it into its *tautomeride*,—



which crystallises from alcohol in red needles decomposing at 195°, and is soluble in cold sodium carbonate. On boiling with caustic potash (10 to 15 per cent) one atom of sulphur is removed as hydrogen sulphide, and replaced by oxygen; the compound, *thioxanthoxalanil*, which is thus formed, crystallises from alcohol in shiny orange plates which decompose at 216—218°, and are soluble in sodium carbonate. The constitution of this substance is either—



or—



it is only decomposed by being heated with concentrated caustic potash (60 to 70 per cent), when oxalic acid and aniline are formed.

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, January 7th, 1907.

Mr. R. J. Friswell in the Chair.

"*The Sixth International Congress of Applied Chemistry at Rome.*" By W. F. Reid, F.I.C., F.C.S.

The author refers in the first instance to the great tendency of modern science towards specialisation, which is accompanied by so large a production of printed matter that personal intercourse between workers has become necessary to mutual agreement. The history of the International Congress of Applied Chemistry is briefly given from the first meeting in Belgium in 1894 down to that in Rome on April 25th of last year. Statistics of the expenditure and membership of the various Congresses are given, showing a very large increase in the last two Congresses. The organisation of such a Congress is described, and particulars of the opening of the Rome Congress by the King and Queen of Italy.

The procedure during the Session is explained, especially with regard to the language difficulty. Details are given of the amount of work done by each of the sixteen Sections and Sub-sections. The resolutions passed by the Congress in plenary sitting are given in detail, most of which refer to the international unification or standardisation of matters or methods connected with industrial chemistry. The invitation given by the British Joint Committee of Scientific Societies for the Congress to meet in London in 1909 is referred to, and the establishment of an Organising Committee here in furtherance of that object described. The entertainments and excursions given to members of the Congress were referred to and illustrated by lantern-slides, some of which were prepared from photographs sent by H.M. the King of Italy for the purpose.

"*The Determination of Higher Alcohols in Spirits.* Part I. *The 'Ester-iodine' Method.*" By G. H. Bedford, and R. L. Jenks (Central Excise Laboratory for India, Kasauli).

The authors point out the defects of the Allen-Marquardt process for the estimation of the higher alcohols in potable spirits. Dunstan and Dymond (*Pharm. Journ.*, xix., [3], 741) have shown how to determine organic nitrites by allowing them to act on an acid solution of potassium iodides in a flask void of oxygen, and then titrating the liberated iodine with thiosulphate. This serves as the basis of the authors' method. Details are given for the extraction and esterification of the total higher alcohols and the subsequent decomposition of the esters by iodine. Beckmann's method of esterification (one part of sodium nitrate and two parts of acid potassium sulphate powdered together) is employed. Results are given showing the accuracy of the method. An analysis can easily be carried out in a day.

"*The Determination of Indigotin in Commercial Indigo.*" By G. Bergtheil and R. V. Briggs.

The authors criticise Bloxam's method for the determination of indigotin (*Journ. Soc. Chem. Ind.*, 1906, xxv., 735), and point out that low results are obtained. The error is due to the factor on which the calculation is based, and the loss of indigotin which invariably occurs in salting out and filtering the sulphonic acid salt. A series of determinations were carried out by the authors' method (*Journ. Soc. Chem. Ind.*, 1906, xxv., 729), and by Bloxam's method (*loc. cit.*), and they are of opinion that the latter does not appear to be reliable either in application to pure indigotin or to commercial indigo. The method is cumbersome and inapplicable to work in the indigo districts of India, owing to the low temperature at which it is necessary to work, and the large amount of ice required for this purpose.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiii., No. 17, December 31, 1906.

Butyric Lactone, and Disymmetric Bimethylated Succinic Glycol.—Louis Henry.—Except for the work by J. Houben entitled "The Reaction of the Organo-magnesium Compounds upon the Lactones" (*Berichte*, 1904), this reaction in connection with the group of internal ethers has not been investigated; M. Henry has therefore made it the subject of his experiments in the case of the simplest of the series, butyric lactone $CH_2—(CH_2)_2—CO$ (with O). This lactone is prepared by the dry distillation of the acid γ-chloro-butyric, $ClCH_2—(CH_3)_2—CO(OH)$. With the methyl-bromide or iodide of magnesium, ethyl acetate produces trimethyl-carbinol and ethyl alcohol:—

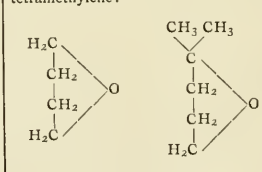
$$CH_3—CO \atop CH_3—CH_2 \!>\! O + 2CH_3.Mg.Br =$$

$$= \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!>\! C—OH—CH_3 + CH_3—CH_2OH ;$$

butyric lactone, which is this ether formed by the fusion into a unitary compound of the two CH_3 groups, changed to CH_2,—

$$\left[\begin{matrix} CH_3—CO \\ CH_3—CH_2 \end{matrix} \!>\! O \right. \quad \left. \begin{matrix} CH_2—CO \\ | \quad\quad | \\ CH_2—CH_2 \end{matrix} \!>\! O \right],$$

ought to give the same products, but re-united into a single molecule, or rather into a unitary compound, *i.e.*, a primary and tertiary glycol, and, in the case of the methyl compounds, disymmetric, bimethylated succinic glycol, $\begin{matrix} H_3C \\ H_3C \end{matrix} \!>\! C(OH)—CH_2—CH_2—CH_2(OH)$. Experiment has fully confirmed these speculations. This glycol is a colourless liquid, thick and viscous, without smell, and with a bitter taste. Boiling-point 158° at 65° mm. Hg, 222° at 774 mm., easily soluble in water, soluble also in iether and acetone, and especially in chloroform; also in benzene slightly warmed; insoluble in petroleum. Submitted to the action of acetyl chloride, this glycol is converted into a chloro-acetine, with the formula $(H_3C)_2—CCl—CH_2—CH_2—CH_2—CH_2(C_2H_3O_2)$; this is a mobile colourless liquid, boiling at 132° at 70 mm., and at 190° at a pressure of 747 mm., whilst giving off hydrochloric acid. The glycol dissolves in fuming HCl, with transformation into its oxide. $(CH_3)_2.C—CH_2—CH_2—CH_2$ (with O). Again, heated with 15 per cent sulphuric acid, bimethylated succinic glycol is transformed into its anhydride, the oxide of bimethyltetramethylene, $\begin{matrix} CH_3 \\ CH_3 \end{matrix} \!>\! C—(CH_2)_2—CH_2$ (with O). Thus, under different conditions, the glycol is readily converted into this oxide, which is a colourless mobile liquid, lighter than water, in which it is insoluble. It boils at 95° under a pressure of 756 mm., and this assigns it a place between tetramethylene and the oxide of symmetric tetramethyl-tetramethylene:—



Boiling-point 67°. Boiling-point 95°. Boiling-point 117°.

A New Silicide of Manganese.—G. Gin.—This new silicide of manganese has been obtained by reduction of rhodomite in the electric furnace. The crystals, separated from the industrial product, gave the following analysis :—

	I.	II.
Manganese	68·64 per cent	69·26 per cent
Iron	4·40 ,,	3·18 ,,
Aluminium	0·74 ,,	0·60 ,,
Silicium	25·02 ,,	25·51 ,,
Carbon	0·16 ,,	0·18 ,,
Sulphur	0·01 ,,	—
Phosphorus	0·01 ,,	—
Losses (not weighed	1·02 ,,	1·27 ,,

Thus the silico-manganese investigated contained about 95 per cent of a crystallised silicide, to which the formula Si_2Mn_3 is given. This consists of beautiful prismatic crystals, very brittle, and fusible at 1250—1300°, attacked by chlorine at a red heat; pure oxygen does not act upon it at the ordinary temperature, but marks the surface towards 500°; gaseous hydracids attack it readily; sulphuric acid has no effect; nitric acid, aqua regia, and hydrochloric acids attack it in the warm, and hydrofluoric acid in the cold. Potassium, the alkaline carbonates, the mixtures of the fused nitrate and carbonate of potassium attack it energetically.

The Solubility of Carbon in the Protosulphide of Manganese.—M. Houdard.—The protosulphide of manganese is of remarkable stability, and, in the presence of carbon, there is no reduction of the sulphide, but simple solution in this compound to the state of graphite. The author has pursued the examination of this phenomenon and made two series of quantitative experiments. 1. A mixture of $MnSO_4$ (anbydrous) 100 grms., and C_4 (charcoal of burnt sugar) 31·78 grms., was heated in the electric furnace to produce the protosulphide. An excess of sugar-carbon corresponding to 10 per cent, *i.e.*, 11·11 grms., was added to the mixture. The only variable factor in this set of experiments was the duration of the operation. The following results were obtained :—

Time.	Percentage graphite dissolved.		Analysis of sulphide	
Mins.	I.	II.	Mn, per cent.	S, per cent.
2 ..	0·0002	0·0007	63·22	36·77
3 ..	0·92	1·01	63·20	36·79
5 ..	1·39	1·40	63·19	35·98
8 ..	1·81	1·87	63·21	36·01
10 ..	2·22	2·24	63·21	36·35
15 ..	2·82	2·85	63·23	36·67
20 ..	3·01	3·21	63·18	36·71
25 ..	3·3c	3·25	63·29	36·70
Theoretical for MnS			63·218	36·782

The conclusions drawn from this table are that the sulphide is not reduced by carbon, and that the solubility of the latter is proportional to the time of heating, other things being constant. The limit of solubility was reached in the two last operations. 2. The bodies resulting from the shorter periods of heating, being full of bubbles (probably from formation of a certain quantity of Co), a second series of experiments was performed by calcination of the carbonate of manganese (perfectly dry) in a current of hydrogen sulphide. The analysis of the product thus obtained gave Mn 63·22 per cent and S 36·78 per cent, and this amorphous sulphide was heated in the furnace with sugar-charcoal in a charcoal boat. The results were as follows :—

Time.	Per cent graphite.		Analysis of sulphide.	
Mins.	I.	II.	Mn, per cent.	S, per cent.
3 ..	1·09	1·20	63·98	36·92
15 ..	2·79	2·80	63·11	36·87
20 ..	3·18	3·20	63·19	36·71
22 ..	3·11	3·12	63·20	35·97
25 ..	3·19	3·20	63·22	36·73

These figures are in accord with those of the first series, giving a maximum solubility of about 3·2 per cent.

Research on the Influence of Radicals on the Character of the Complementary Valencies of Oxygen.—M. Tchelinzef.—According to the researches of Blaise, the organo-magnesium compounds produced by the action of sulphuric ether upon organo-magnesium combinations of the type RMgI may be subdivided into two classes, the monoetherates, $RMgI.1(C_2H_5)_2O$, and the di-etherates, $RMgI.2(C_2H_5)_2O$, the formation of which may be attributed to the complementary atomicities possessed by the oxygen in ordinary ether. These complex bodies resemble, on the one hand, the bodies resulting from the action of the simple ethers upon the halogen acids, and, upon the other, the combinations of ether with magnesium iodide. For each of these classes of compounds are known the two series :—

$$HV.1(C_2H_5)_2O \text{ and } HV.2(C_2H_5)_2O;$$

$$Mg<^{I.1(C_2H_5)_2O}_{I.1(C_2H_5)_2O} \text{ and } Mg<^{I.2(C_2H_5)_2O}_{I.2(C_2H_5)_2O}.$$

These analogies favour the hypothesis according to which ether, in the organo-magnesium combinations, joins itself to the part of the molecule containing the haloid element. These considerations have led the author to attribute a similar constitution to the complex bodies formed by ether and the organo-magnesium radicles. The hypothesis of the existence of the complementary valencies of the oxygen may be equally extended to the di-etherates. The investigations pursued on these lines were based upon the thermal effect accompanying the reaction. The results obtained were as follows :—

Formula of ether.	$RMgI+R_2O$. q.	$RMgIR_2O+R_2O$. q'.	$Q=q+q'$.	Q found directly.
$C_2H_5.O.C_2H_5$..	6·63	6·16	12·79	12·60
$C_3H_7.O.C_2H_5$..	6·15	5·93	12·08	12·12
$i\,C_4H_9.O.C_2H_5$..	5·84	5·37	11·21	11·40
$i\,C_5H_{11}.O.C_2H_5$.	6·17	5·47	11·64	11·73
$i\,C_5H_{11}.O.C_5.H_{11}$	5·91	4·54	10·45	10·31
$C_6H_5.O.CH_3$ ..	—	—	—	—
$C_6H_5.O.C_2H_5$..	—	—	—	—

It follows from these figures that, judging by the thermal effect produced, the replacing of radicals by one another in the ethers of the fatty series modifies very slightly the character of the complementary valencies of the oxygen; but the introduction of the isoamyl group is followed by a still slighter evolution of heat. The nature of the reaction with the aromatic radicals is totally different, the thermic effect following the introduction of a phenyl radical being almost null. The complementary values of nitrogen are seen from the following data (from Thomson, Gauthier and Vignon) to present a similar phenomenon, with reference to the heat disengaged by the addition of certain acids to the tertiary amines :—

Formula of the tertiary amine.	HCl.	H_2SO_4.	$\frac{1}{2}H_2SO_4$.
$N(C_2H_5)_3$	9·5	—	—
$N(CH_3)_3$	8·3	21·8	10·3
$N(C_2H_5)(CH_3)_2$	6·8	15·2	7·6
$N(C_6H_5)_3$	0	0	0

Thus there is a similitude of properties between O and N, represented thus :—

$$\begin{matrix}R\\R\end{matrix}>O+<^{X}_{MgR} \quad \text{and} \quad \begin{matrix}R\\R\\R\end{matrix}>N+<^{X}_{H}.$$

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 15, 1906.

Benzoyl Nitrate, a New Nitrating Agent.—Francis Francis.—When silver nitrate acts on benzoyl chloride at a low temperature (about −15°) a yellow oil separates out. The equation is—

$$C_6H_5.CO.Cl+AgNO_3=C_6H_5.CO.O.NO_2+AgCl,$$

and the yield is almost quantitative. The oil is freed from silver salts by filtering through dry asbestos, care being taken to exclude all trace of moisture. If benzoyl nitrate is filtered through paper which has not previously

been dried an explosion occurs, the equation of the reaction being $C_6H_5.CO.O.NO_2 + H_2O = C_6H_5.COOH + HNO_3$. When it is cautiously heated to 100°, NO_2 and oxygen are evolved. The nitrate is characterised by the ease with which it exchanges its NO_3 group for hydrogen, and it is therefore applicable as a nitrating substance. It can be used either as such or in solution. It is best either to add a known volume of the nitrate to an excess of the substance to be nitrated, at the same time cooling or to work with the latter diluted with carbon tetrachloride if the reaction proceeds too energetically. The benzoic acid formed during the reaction must be removed by a solution of caustic or carbonic alkali. The author has investigated many such nitration processes, and finds that the great advantage in using benzoyl nitrate is due to the fact that the operation can be performed in absence of water.

Velocity of the Addition of Bromine to Cinnamic Acid.—W. Herz and Bruno Mylius.—When bromine is added to a solution of cinnamic acid in chloroform the reaction which occurs is—

$C_6H_5.CH:CH.COOH + Br_2 = C_6H_5.CHBr.CHBr.COOH$.

In studying the velocity of this reaction the authors added titrated solutions of bromine in chloroform to cinnamic acid solutions of known strength contained in test-tubes. The test-tubes were then fused up, and the mixture kept at 25°. After definite periods the tubes were opened under potassium iodide solution, and the iodine corresponding to the unused bromine titrated with sodium thiosulphate solution and starch. They found that the equation of a bimolecular reaction, $\frac{1}{t(A-B)} \log \text{nat} \frac{B(A-x)}{A(B-x)} =$ constant, holds good, A being the weight of cinnamic acid in 20 cc., B the weight of bromine in 20 cc., x the weight of substance used up, and t the time (in hours). Then other substances were added, *e.g.*, bromoform, iodine, &c. It was found that the former has no influence upon the velocity of the reaction, while the latter acts catalytically, the constant being ten times greater when iodine is added than when it is not. When carbon tetrachloride is used as solvent the constant is about three times as large as with chloroform, but the latter is much the more convenient in use.

Decomposition of Grape-sugar with Zinc Hydroxide-ammonia in presence of Acetaldehyde.—A. Windaus.—When acetaldehyde is added to a solution of grape-sugar in zinc hydroxide-ammonia, besides α-methyl-imidazol $\alpha\mu$-dimethyl-imidazol results. The constitution of this unknown imidazol was determined synthetically. It is formed from grape-sugar only on artificial addition of acetaldehyde, and if the latter is absent only monomethyl-imidazol results. Hence when grape-sugar is split up by hydroxyl ions in presence of ammonia, methyl glyoxal and formaldebyde are formed, but not acetaldehyde. The fact that grape-sugar can be split up by dilute alkalis under special conditions into acetaldehyde and formic acid is explained by supposing that when ammonia is present the intermediate substance (which yields acetaldehyde and formic acid) is caught by the ammonia, and converted into stable condensation products. The intermediate product is methyl glyoxal.

New Method of Nitrating.—Otto N. Witt and Alfred Utermann.—The general method of nitrating aromatic compounds is the addition of nitric acid together with some substance which will remove water, *e.g.*, sulphuric acid. The addition of this last often affects the position of the nitro group, and in cases where several isomers are simultaneously formed the relative quantities of the products are much altered. This is well shown in the case of aniline or acetanilide. The authors have studied the nitration of these substances, completely excluding all strong mineral acids, and using acetic anhydride to remove the water formed, and glacial acetic acid as solvent. To separate as accurately as possible the isomers contained in the raw product, distillation in a current of steam was employed. It was found that when aniline is nitrated by this method, to one part of the para compound not less than three parts of the ortho compound were formed.

Action of Hydrocyanic Acid upon Aldehyde Ammonia.—Giacomo Ciamician and P. Silber.—When dilute (3 per cent) hydrocyanic acid acts upon aldehyde ammonia slowly in the cold the results are very different from those obtained when concentrated solutions are used and heat is applied. The most important products are the two isomeric α-imidodipropionic acids; the A-α-acid melts at 255°, and the B-α-acid at 235°. The properties of the two acids are shown by the following table:—

Compounds.	A-α-Imidodipropionic acid.	B-α-Imidodipropionic acid.
Acid.	M.p. 254—255°.	M. p. 234—235°.
Acid barium salt.	Needles.	Gelatinous.
Neutral barium salt.	Sol. in cold water.	Insol. in cold water.
Silver compounds.	$C_6H_{10}O_4NAg + AgNO_3$.	$2C_6H_{10}O_4NAg + AgNO_3$.
Neutral silver salt.	Gelatinous ppt.	Powdery ppt.
Diethyl ester.	B. p. 123—124° at at 15 mm.	B. p. 121—122° at 15 mm. M. p. −5°.
Nitroso compound of diethyl ester.	B. p. 177° at 18 mm.	B. p. 163—164° at 17 mm.
Monamide.	$C_6H_{12}O_3N_2$. M. p. 232°.	$C_6H_{12}O_3N_2 +$ M.p. 210°. $1\frac{1}{2}H_2O$.
Imide.	—	M. p. 186°.
Nitrile.	M. p. 68°.	—

The isomerism of the two acids corresponds to that of the racemic and meso-tartaric acids; probably the A-acid is the racemic and the B-acid with the lower melting-point the inactive form.

MISCELLANEOUS.

Institute of Chemistry.—*Examinations in Chemical Technology*.—The next examinations in Chemical Technology will commence on Tuesday, April 23rd, 1907. The examinations will be open only to Fellows, and to those Associates who have been registered as such for at least one year, who produce evidence of practical technological training. Fellows and Associates who desire to present themselves are required to send in their applications and fees not later than Tuesday, February 26th, 1907. The Examination will be both written and oral, and will not extend over more than four days. The candidate is required to name some important industry, upon which his knowledge of the subjects of the Examination will be tested. The Examiners will take into account original work and special knowledge, but not so as to excuse the candidate from any part of the Examination.

NOTES AND QUERIES.

Beetroot Sugar.—A correspondent wishes to be told the best books on the beetroot sugar industry.

Fluor-spar.—Can anyone say what use is now being made of fluor-spar, for which there is said to be a great demand at the preseot time?

MEETINGS FOR THE WEEK.

TUESDAY, 22nd.—Royal Institution, 3. "The Sculpture of Aegina in Relation to Recent Discovery," by Prof. Percy Gardner, Litt.D., &c.

WEDNESDAY, 23rd.—Society of Arts, 8. "The Isthmus of Panama," by Philippe Bunau-Varilla.

THURSDAY, 24th.—Royal Institution, 3. "Recent Advances in the Exploration of the Atmosphere," by W. N. Shaw, M.A., &c.

—— Society of Arts, 4.30. (Indian Section)

FRIDAY, 25th.—Royal Institution, 9. "The Guildhall Library." by Charles Welch, F.S.A.

SATURDAY, 26th.—Royal Institution, 3. "Latest Phases of Music" (with Musical Illustrations), by Sir Alexander C. Mackenzie, Mus. Doc., &c.

THE CHEMICAL NEWS.

Vol. XCV., No. 2461.

NIOBIUM, TANTALUM, AND TITANIUM:

Observations on.

By W. B GILES, F.I.C.

(Continued from p. 3).

The first object, that is to say, effecting the reduction of the acids as quickly as possible, is solved by replacing the rod, sheet, or granulated zinc by zinc-dust, or by the spongy zinc obtained by the electrolysis of zinc solutions. (In the same way spongy tin or copper may be employed). The saving of time that is effected in this manner is so remarkable that no one who has tried the two varieties of metals will ever revert to the use of the compact forms again. It is no exaggeration to say that by the use of the finely divided metals better results can be obtained in a few minutes than are possible in many hours when using the granulated form.

But this is not the only advantage; the finely divided metals react and enable reductions to be effected with many solutions (*e.g.*, those with organic acids) which have little or no action upon compact metals. The second object is to present the three acids to the reducing agents *in a soluble form*, and when these two conditions are combined it will be seen that one can easily detect a very small amount of niobium mixed with either tantalic or titanic acid. The Schöene-Weller test for titanium (hydric peroxide), enables us to detect small amounts of this metal in presence of either of the others, and the only thing lacking is some process which will indicate tantalum with as much certainty when associated with the other two metals. It would appear, however, that up to the present time no direct test for tantalum is known by which it may be unmistakably identified when it is mixed with large quantities of the other acids. It is to be hoped that one may be discovered. In reference to this subject, the author has not been able to obtain good results by the process given by Dr. A. A. Nnyes (Chemical News, vol. xciii., p. 180).

Trials have shown that freshly precipitated and undried tantalum hydroxide, whether alone or mixed with niobium or titanium, dissolves rather freely in a solution of hydrochloric or sulphuric acid, to which hydrogen peroxide has been added. Dr. Noyes's description of the process is:—"That tantalum hydroxide, whether present in small or large quantity, whether alone or with much titanium, remains in large part (about one-half) undissolved by this solvent." No explanation of this curious statement that "about one-half" of the tantalic acid declines to go into solution is given. Why should half the tantalic dissolve and the other half remain insoluble? One would almost infer that either the amount of peroxide of hydrogen or the hydrochloric or sulphuric acid used was insufficient. Direct trials with some of the mixed hydrated acids derived from columbite from Middleton, Connecticut, and also with those from Australian tantalite (sp. gr. 7·24) showed that they dissolve completely when diffused in dilute hydrochloric or sulphuric acid on addition of *sufficient* pure hydrogen peroxide (Merck's "perhydrol").

The solution is much assisted by *gentle* warming. It is possible that tantalic hydroxide is *more slowly* soluble than the corresponding niobic and titanic hydrates, but even if this is the case, the formation from the precipitate of insoluble oxyfluorides as a confirmatory test for the presence of tantalum cannot be regarded as decisive, for Kriss and Nilson (*Ber.*, 1881, p. 1676) showed that niobium potassium oxyfluoride gives a similar insoluble compound on boiling its solution, which they analysed and found it to be a potassium niobium dioxyfluoride; so that this test does not appear to afford a certain proof of the presence of tantalum. The most decided difference which the author has yet found in the behaviour of the three metals (apart from the double potassium fluorides) lies in *the remarkable insolubility of tantalum in potassium binoxalate in cold solutions*. If 1 grm. of pure ignited tantalic acid is fused with 2 grms. of pure potassium carbonate at a *high* temperature, it yields a perfectly clear fluid fusion; this dissolves in water to a perfectly clear solution. If to this is added 4 grms. of pure crystallised oxalic acid on making the liquid up to about 50·0 cc. and heating to boiling a perfectly clear solution is obtained, which is then made up to 100·0 cc. with hot water. On cooling and standing for twenty-four hours, the solution, when 100·0 cc., becomes quite thick and opaque, and deposits a large quantity of precipitate resembling ammonium magnesium phosphate. If the solution has only been made up to 50·0 cc. the solution becomes so solid on cooling (like blanc-mange) *that the flask may be inverted without spilling a drop*. If exactly the same weights of niobic and titanic are treated in the same manner, and made up to 100·0 cc., the solutions show nothing similar; they remain clear, at least for several days. When the thick tantalum solutions are heated they become perfectly clear again. This remarkable difference leads the author to hope that a further investigation of this matter (in which he is now engaged) may lead to some useful qualitative and possibly quantitative methods for the estimation and separation of tantalum.

In searching for soluble salts of the three metals, and such as are suitable for use with reducing agents, the number is seen to be but small. The fluorides are objectionable because they cannot be dealt with properly in glass vessels. Wollaston showed that the hydroxides of the metals were soluble in oxalic, citric, and tartaric acids, or in their acid salts, and since then racemic and lactic acids have been used as good solvents. Of these compounds only those with oxalic and citric acid have been tested, and of these two the oxalic compounds have been found, generally speaking, to be the most useful. These organic acids have one great drawback, and that is that they act as reducing agents themselves upon most oxidising bodies, and so they cannot find much application in quantitative work, but for qualitative purposes they are very useful.

After a great number of experiments the author could only find one suitable inorganic acid (excepting hydrofluoric) with which it is possible under some conditions to obtain fairly soluble salts. This was phosphoric acid, and it is somewhat remarkable that nearly all the acids yielding the most soluble salts of tantalum, niobium, and titanium are polybasic acids.

The hydroxides used in the following tests were obtained in a pure condition as follows:—The tantalic acid was made from twice re-crystallised tantalum-potassium fluoride, which was then precipitated with ammonia, the well washed precipitate re-dissolved in pure hydrofluoric acid; this solution precipitated again with ammonia barely to the neutral point, the precipitate thoroughly washed by decantation, dried, and ignited at a high temperature. It then only contained a very minute and just detectable amount of niobic acid, but appeared to be absolutely free from titanic acid, although the salt at the start contained a decided amount of the latter body. The niobic acid was prepared from well crystallised potassium fluoxyniobate; this also on starting was found to contain no inconsiderable amount of titanium. The salt was dissolved in water and well boiled, filtered from the insoluble matter, and then when cold the filtrate was precipitated with ammonia barely to the neutral point. The precipitate was thoroughly washed by decantation, and then re-dissolved in pure hydrofluoric acid; this solution was then diluted, and precipitated again with ammonia barely to the neutral point; the precipitate was then well washed by decantation, dried, and ignited at a high temperature.

Titanic acid was prepared from rutile by Wöhler's process; the titanic acid prepared from the well crystallised double fluoride by ammonia was snow-white; it was not dried but was preserved as a stiff paste.

In the following tables it is endeavoured to give as nearly as possible *the exact amount* of the strengths and quantities of the solutions and the reagents employed in order that the results may be repeated by any one who has an interest in the matter. Hence, such expressions as "a few drops," "enough," "an excess of," and the like are avoided.

Preparation of the Solutions.

Tantalum phosphate solution was made by taking 1 grm. pure ignited tantalic acid, fusing with 2 grms. of pure potassium carbonate at a very high heat till the fusion was clear, dissolving in water (the solution should be quite clear); to this adding 20·0 cc. of 1700 sp. gr. phosphoric acid, heating over a low flame till the mixture was much concentrated and appeared quite clear; when cold diluted with water up to 100·0 cc. This solution, at first perfectly clear, can be kept for a day or two, but gradually goes opalescent and turbid. The strong syrupy solution can be kept clear for a long time.

Tantalum oxalate solution is made exactly as above described, except that a solution of 4 grms. of pure oxalic acid is employed instead of phosphoric acid. The solution is made up to 100·0 *cc. when hot and clear*: it must be also *measured hot*, as it deposits greatly on cooling.

Niobium phosphate solutions are prepared precisely in the same way as the tantalum phosphate, only substituting 1 grm. of niobic anhydride for the tantalic anhydride; they do not keep long clear when diluted, but the concentrated syrupy solution will keep unaltered for a long time.

Niobium oxalate solution is made as the phosphate, from 1 grm. of ignited acid, 2 grms. of potassium carbonate fused together, and the clear solution heated with 4 grms. of pure oxalic acid. This solution keeps well, and if it deposits a trifle in cold weather it goes into solution again on warming.

Titanium Phosphate.—As titanium does not form soluble salts with the alkalis, and as the acid salts are difficultly soluble in phosphoric acid, this is made by dissolving titanic hydrate (which must not have been heated or dried) in the form of paste in *cold* strong phosphoric acid. The amount of titanic anhydride in the paste is ascertained by careful drying and ignition. Then an amount equal to 1·0 grm. of the anhydride is weighed out and dissolved in 20·0 cc. of 1700 sp. gr. phosphoric acid, and made up to 100·0 cc. This diluted solution does not remain clear for more than a few hours; it appears less stable than any of the other dilute phosphate solutions, but the strong solutions appear to remain unaltered for weeks.

Titanium oxalate solutions are made by dissolving titanic hydrate in hot potassium binoxalate and crystallising. The well defined crystals contain 22·5 to 23 per cent of titanic anhydride; the amount which is equivalent to 1 grm. of this is ascertained, and made up to 100·0 cc.; this solution keeps well, and only deposits slightly in cold weather.

Tests of the Niobium Oxalic Solutions.

1. Taken 10·0 cc. = 0·1 grm. Nb_2O_5. Added 1 grm. crystallised Ox, and boiled; then added 1 grm. zinc-dust. Result, *immediately*, a rich very strong brown colour almost *opaque* to transmitted light.

2. Taken 1·0 cc. = 0·01 grm. Nb_2O_5. Added 9·0 cc. water, 1 grm. crystallised Ox, and boiled; then added 1 grm. zinc-dust. Almost immediately a rich strong yellowish brown colour.

3. Taken 0·1 cc. = 0·001 grm. Nb_2O_5. Added 10·0 cc. water, 1 grm. crystallised Ox, and boiled; then added 1 grm. zinc dust. Almost at once a very decided brown colour; this fades away quickly when the zinc-dust settles, but the colour can be restored by shaking up again; the solution should *not* be boiled after adding the zinc-dust. Evidently less than this amount could be detected.

4. Taken 10·0 cc. = 0·1 grm. Nb_2O_5. Added 1·0 cc. concentrated H_2SO_4; then zinc-dust. Solution becomes dark brown, then black, opaque to light.

5. Taken 1·0 cc. = 0·01 grm. Nb_2O_5. Added 9·0 cc. of water, and 1 cc. of H_2SO_4; added zinc-dust. Solution quickly becomes dark brown, then black; by transmitted light is seen to be of a brown-yellow hue.

6. Taken 0·1 cc. = 0·001 grm. Nb_2O_5. Added 10·0 cc. water and 1 cc. of H_2SO_4; added zinc-dust. This only gave a slight darkening on long contact. Not as delicate as No. 3.

7. Taken 10·0 cc. = 0·1 grm. Nb_2O_5. Added 1·0 cc. of 20 per cent pure hydrogen peroxide. Result, a faint straw-coloured solution equal to about one-fifth of a mgrm. of TiO_2.

Tests of the Niobium Phosphate Solutions.

8. Taken 10·0 cc. = 0·1 grm. Nb_2O_5. Heated to boiling, and added 1 grm. of zinc-dust. Result, *at once, an intensely black ink-like solution*, opaque to light.

9. Taken 1·0 cc. = 0·01 grm. Nb_2O_5. Added 2·0 cc. H_3PO_4 (sp. gr. 1500), and 7·0 cc. water, with 1 grm. zinc-dust. Almost immediately a black coloured solution; by transmitted light looks brown-red.

10. Taken 0·1 cc. = 0·001 grm. Nb_2O_5. Added 2·0 cc. H_3PO_4 (sp. gr. 1500), and 8·0 cc. water, boiled up, and then added zinc-dust, 1 grm. Distinct reaction, solution becomes dark and of a brownish colour. Takes about half-an-hour to develop.

11. Taken 10·0 cc. = 0·1 grm. of Nb_2O_5. Added 1·0 cc. of 20 per cent peroxide of hydrogen; slight but distinct pale yellow colour, equal to about one-third mgrm. TiO_2; more delicate than No. 7.

Tests of the Tantalum Solutions.

12. Taken 10·0 cc. tantalum phosphate, equal to 0·1 grm. Ta_2O_5. Boiled, added 1 grm. zinc-dust. No change.

13. Taken 10·0 cc. tantalum phosphate. Added 1 cc. of 20 per cent H_2O_2. No change; solution remains white.

14. Taken 10·0 cc. tantalum oxalate = 0·1 grm. Added 1·0 cc. of 20 per cent H_2O_2. No change; solution white.

15. Taken 10·0 cc. tantalum oxalate solution = 0·1 grm. Boiled, and added 1 grm. of zinc-dust. A very faint slight yellow shade, indicating a trace of niobium.

Tests of the Titanium Potassium Oxalate Solutions.

16. Taken 10·0 cc. = 0·1 grm. TiO_2 + 1 grm. crystallised Ox, boiled, then 1 grm. zinc-dust added; gave at once strong brown-yellow colour, not nearly as deep, however, in colour as the niobium (No. 1). When action is over solution looks like a saturated solution of $PtCl_4$.

17. Taken 1·0 cc. = 0·01 grm. TiO_2 + 1 grm. crystallised Ox + 9·0 cc. water, boiled, and then 1 grm. zinc-dust added and well shaken. Gave a strong yellow colour like saturated solution $K_2O.2CrO_3$.

18. Taken 0·1 cc. = 0·001 grm. of TiO_2 + 1 grm. crystallised Ox + 10·0 cc. of water, boiled, and then 1 grm. zinc-dust added, gave a light yellow solution, quite distinct.

19. Taken 10·0 cc. = 0·1 grm. of TiO_2 + 1·0 cc. of pure H_2SO_4. Added 1 grm. zinc-dust; *not* boiled; gave at once a *dark brown* colour. On standing some hours this changed to a purple or violet colour of much lighter hue.

20. Taken 1·0 cc. = 0·01 grm. of TiO_2 + 1·0 cc. of pure H_2SO_4 + 8 cc. of water + 1 grm. zinc-dust, *not* boiled; gave from the first a weak pale violet colour, at no stage brown. This solution, though ten times as strong as No. 18, is not as delicate.

21. Taken 10·0 cc. = 0·1 grm. TiO_2. Added 1·0 cc. 20 per cent H_2O_2. Deep orange colour at once like saturated $K_2O.2CrO_3$.

22. Taken 1·0 cc. = 0·01 grm. TiO_2. Added 1·0 cc. of 20 per cent H_2O_2. Bright yellow solution, like saturated potassium chromate.

23. Taken 0·1 cc. = 0·001 grm. TiO_2 + 1 cc. of 20 per cent H_2O_2. Bright yellow solution, evidently much less could be detected, but the colour in Nos. 21, 22, 23 is not so deep as in the phosphoric acid solutions of the same strength.

Tests of the Titanium Phosphoric Acid Solutions.

24. 10·0 cc. = 0·1 grm. TiO_2, gently heated, and then 1·0 grm. of zinc-dust added, gives a beautiful violet colour solution.

25. 1·0 cc. = 0·01 grm. TiO_2 + 9·0 cc. water heated to a boil, and then 1 grm. zinc-dust added, nearly all the TiO_2 precipitated apparently *as hydrate*; this was reduced on standing to a lilac coloured precipitate.

26. 1·0 cc. = 0·01 grm. TiO_2 + 2·0 cc. of 1500 sp. gr. H_3PO_4 + 7·0 cc. water, heated just to boil, and 1 grm. of zinc-dust added, gave a faint but still very distinctly coloured lilac solution. Weaker solutions were not tried, as this tint was so faint.

27. 10·0 cc. = 0·1 grm. TiO_2 + 1·0 cc. of 20 per cent H_2O_2. Immediate, deep orange colour.

28. 1·0 cc. = 0·01 grm. TiO_2 + 1·0 cc. of 20 per cent H_2O_2. Bright yellow colour, like saturated potassium chromate.

29. 0·1 cc. = 0·001 grm. TiO_2 + 1·0 cc. of 20 per cent H_2O_2. Light bright yellow solution, evidently much less could be detected. Note, Nos. 27, 28, 29 are considerably deeper in colour, and therefore more delicate than Nos. 21, 22, 23.

Summary of the Qualitative Tests.

Tantalum solutions, whether in oxalic or phosphoric acid, give no coloration when treated with zinc-dust as described.

Niobium solutions, both in oxalic or phosphoric acid, give deeply coloured solutions when treated with finely-divided zinc. These are *always either black, brown, or yellow*, according to the amount of dilution, but *never blue or violet*, providing a sufficient amount of free oxalic or phosphoric acid is present.

Titanium solutions *in oxalic acid* give reactions and colorations when reduced with zinc-dust much resembling those yielded by niobium, except that they are somewhat lighter in colour, but the solutions *in phosphoric acid always give violet or lilac coloured hues, and never black, brown, or yellow*, if sufficient free phosphoric acid is present.

In this way tests Nos. 1 and 8 will detect a very small amount of niobium mixed with tantalum, while Nos. 8 or 9 and 24 or 26 show a very marked difference between niobium and titanium. It has been noted that solutions of titanic acid in phosphoric acid are more sensitive when tested with hydrogen peroxide than the corresponding solutions in oxalic acid.

(To be continued).

THE EFFECT OF TEMPERATURE ON THE ACTIVITY OF RADIUM AND ITS TRANSFORMATION PRODUCTS.

By HOWARD L. BRONSON, Ph.D.

Introduction.

A LARGE number of investigators have attempted to alter the activity of various radio-active substances by subjecting them to very high and also to very low temperatures. Among all these attempts only two, as far as the writer is aware, have apparently given positive results.

Curie and Danne (*Comptes Rendus*, 1904, cxxxviii., 748) found that the rate of transformation of the active deposit from radium was apparently permanently increased, after it had been subjected to temperatures above 800° C. The writer repeated these experiments, and showed that this apparent increase was due to the volatilisation of radium B (*Am. Journ. Sci.*, July, 1905; *Phil. Mag.*, January, 1906). By having the active deposit sealed in a glass tube when heated, it was shown conclusively that the rate of transformation had not been permanently altered by temperature up to 1100° C. In both the above experiments the rate of transformation was determined in the cold after the active matter had been removed from the furnace, and no attempt was made to detect any change in the activity of the active deposit, while it was actually at a high temperature.

Results obtained by Makower.

Makower has more recently made some further investigations on the same subject (*Proc. Roy. Soc.*, March, 1906). He concludes:—"The results show clearly that the activity, as measured by the β and γ rays, can be changed by high temperatures, the observed effects being *consistent* with the explanation offered by Curie and Danne, that the rate of decay of radium C is increased by high temperatures." The method employed by Makower differed from that employed in the previous experiments, in that he subjected radium emanation (which was in a state of radio-active equilibrium) to the high temperature, instead of merely the active deposit. The emanation was sealed in a quartz tube, so that no volatile product could escape. This method had this advantage—that although the measurements were also taken when the tube was cold, yet it was possible to detect changes in the activity which had occurred during the time of heating. The activity of the quartz tube was always found to be diminished after it had been heated to 1000° C. or over. The amount of decrease varied from 3 to 15 per cent, depending on the temperature and length of time of heating. On account of the presence of the emanation, the activity recovered its normal value again after about one hour, apparently showing that, after heating, the rate of production of the active deposit was greater than the rate of decay. No light, however, was thrown on the question, investigated by Curie and Danne and the writer, as to whether the rate of decay of the active deposit had been *permanently* altered or not.

The arrangement of the apparatus employed by Makower is shown in Fig. 1. The ionisation in the testing vessel was produced by both β and γ rays, and it is easily seen that the distribution of the active deposit in the quartz tube might have considerable effect on the observed activity. It is also to be noticed that no change in the activity took place until a temperature of about 1000° C. was reached, which is about the temperature at which radium C begins to volatilise.

As all the results obtained by Makower can be satisfactorily explained on the assumption that radium C volatilised and deposited itself near the ends of the tube, it seemed desirable to further test the effect of high temperatures on the activity of radium and its transformation products under quite different experimental conditions.

Apparatus and Method.

The arrangement of the apparatus, as used in the following experiment, is shown in Fig. 2. A few tenths of a milligrm. of pure radium bromide was sealed in a quartz tube, under diminished pressure, and placed in a small electric furnace directly below the electroscope, as shown in the figure. In order to protect the electroscope from convection currents of air, it was entirely surrounded by another vessel and separated from the furnace by two layers of asbestos and one of lead, with air spaces between them. In addition to this, the air between the furnace and the electroscope was continuously removed by an electric fan, not shown in the figure. Even with these precautions the gold leaf did not move with perfect regularity, but the errors due to this fact were very small, as can be seen from the observations plotted in Fig. 3.

After several unsuccessful attempts, a satisfactory platinum resistance furnace was constructed, with which a temperature above 1600° C. was obtained. The construction of the furnace is shown in the figure. The inside cylinder was a platinum tube, which was surrounded by a layer of magnesium oxide in which the platinum wire was embedded. Surrounding the magnesium oxide was a porcelain tube, which in turn was covered with a thick layer of asbestos.

* Read before the Royal Society, November 15, 1906.

The temperature was measured by a platinum-rhodium thermo-couple and a potentiometer specially designed for such measurements by Professor H. M. Tory. The couple was calibrated up to 1100° by comparison with one of Dr. Barnes' platinum resistance thermometers, which had been carefully standardised. The calibration curve was extended beyond 1100° by means of an equation given by Le Chatelier. This equation is of the form $\log e = a \log t + b$,

The arrangement of the apparatus as described above furnishes certain favourable experimental conditions to which attention should be called. Errors due to change in the distribution of radium C were largely avoided by making the quartz tube short (about 4 cm.), in comparison with the diameter of the electroscope (about 12 cm.), and by measuring the activity entirely by the γ-rays. Any possible error introduced by the decay of the emanation

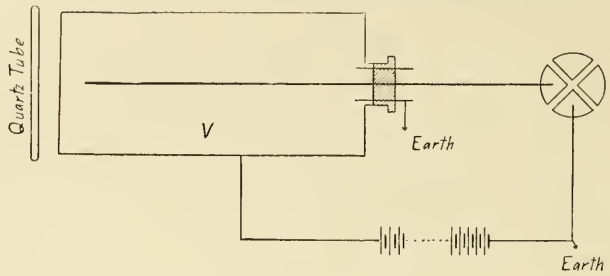


FIG. 1.

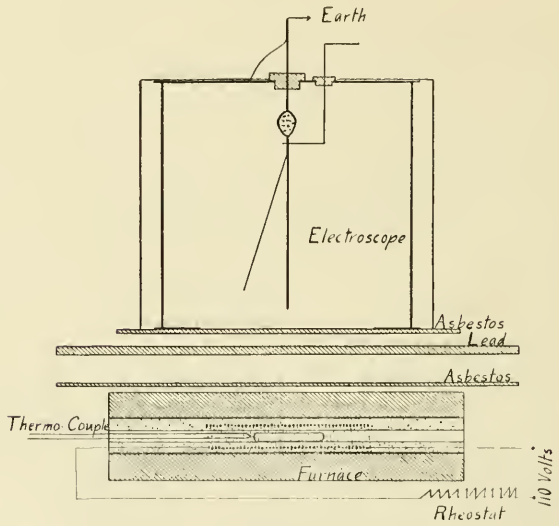


FIG. 2.

where e is expressed in micro-volts. This equation, with suitable constants, fitted the calibration curve almost perfectly below 1100°. In order to make certain that it held true for higher temperatures, the melting-point of platinum was directly determined, and was found to differ from the calculated value by less than 10°.

The relative position of the quartz tube and thermo-couple in the furnace is shown in the figure. It is easily seen that the temperature of the couple is certainly not higher than that of the quartz tube. It is therefore evident that the values given for the temperatures in this paper are certainly not too high.

was avoided by the use of radium itself as the active substance. The relative position of the quartz tube and the electroscope remained absolutely unchanged throughout the entire experiment. The *great* advantage, however, of the above arrangement lay in the fact that measurements of activity and temperature could be taken simultaneously. This made it possible instantly to detect any change in the activity of radium C., as its temperature was raised.

The importance of this point becomes evident, when we consider the complexity of the problem under investigation. This complexity arises from the fact that there were five radio-active substances in equilibrium, sealed together in

the quartz tube. Since the writer has shown that the rate of transformation of the active deposit is not permanently altered by subjecting it to temperatures up to 1100° C., the only explanation of the decrease of activity observed by Makower is that the equilibrium quantity of radium C at high temperatures is less than normal. A number of special cases will perhaps make this point more evident.

For simplicity we will assume that in any particular case only one of the active substances is affected by the temperature. For example, suppose that at a certain definite temperature the rate of transformation of radium C is suddenly increased, the electroscope will show a sudden increase in the activity. This increase in activity will not be permanent, but will gradually diminish and practically disappear after three hours. This follows from the fact that, when equilibrium is reached, the number of atoms of radium C, which break up per second, must be the same as the number supplied, and this number, according to our assumption, has not been changed. If now after equilibrium is reached at this temperature, the active matter is removed from the furnace and its activity measured again at ordinary temperature, it will be found to be less than normal, since the number of atoms of radium C present is less than the normal number. As a second example, suppose that the rate of transformation of radium B is suddenly increased. At once the activity of radium C begins to rise, reaches a maximum in about thirty-five minutes, and decays to its normal value again in about three hours. An increase in the rate of transformation of the emanation would produce similar results, except that it would take about three hours for the activity of radium C to reach a maximum, and as much as three or four weeks to decay to its normal value again. With radium A the case is quite different. Its rate of transformation is so rapid that it would regain its equilibrium value very quickly. Therefore, unless a very large change in its rate of transformation took place, the effect on the activity of radium C would be very small and difficult to detect. On the other hand, the rate of transformation of the emanation is so slow, that any change in the activity of radium would not appreciably affect the activity of radium C for several hours, and could not possibly be detected in the present experiment. The above discussion is all based on the assumption that the activity is being measured by the penetrating γ-rays, which come entirely from radium C.

It is thus clearly seen not only that it should be possible to determine the effect of high temperatures on the activity of the emanation and the active deposit, but that the particular substances affected ought also to be determined by the way in which the activity, as measured by the γ-rays, changes.

Observations.

When the apparatus was once arranged, as explained above, it was a very short simple operation to perform the experiment. Simultaneous observations of activity and temperature were taken at intervals of two or three minutes. The temperature of the furnace was raised gradually up to about 1300° C. It was allowed to remain between this temperature and 1350° for over an hour, and then gradually raised again to 1500°. After keeping it at about this temperature for nearly another hour, it was raised again to over 1600°. At about this temperature two difficulties were encountered, the insulation of the furnace failed, and the emanation began to escape from the quartz tube. The slightly increased activity shown by the last observation (Fig. 3) was due to this escape of the emanation and its presence around the electroscope. The furnace was then allowed to cool. Its activity measured several hours later was found to be less than half its original value. That this decrease in activity was actually due to the escape of the emanation was shown by the fact that the quartz tube regained about half its lost activity during the next four days.

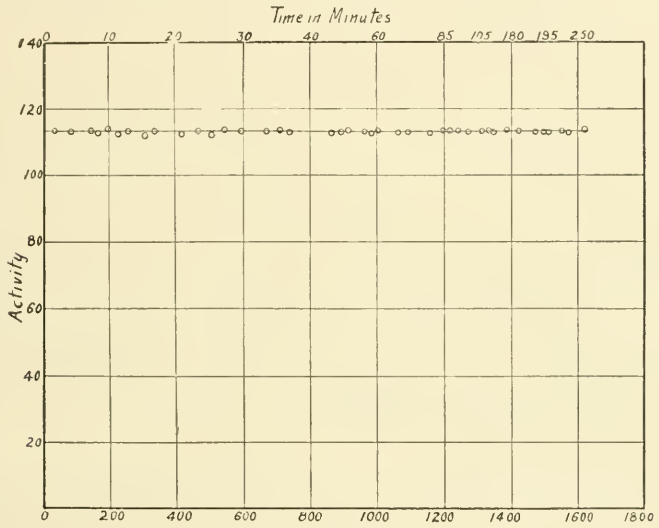


Fig. 3.

Fig. 3 shows the results of the series of observations above described. The approximate times at which the

measurements were taken are given at the top of the figure. Below 1200° each point in general represents a single observation, while above this temperature most of them represent a mean of several, which accounts for their greater regularity. There is no evidence of any change in the activity as measured by the penetrating γ-rays. If any change at all took place, it was certainly less than 1 per cent.

The length of time during which the temperature of the furnace was above 1500° was sufficient to have made it possible to detect a 1 per cent variation in the rate of transformation of either the emanation or radium B, but there was no evidence of any such change. A similar set of observations taken with decreasing temperatures also failed to reveal any change in the activity.

Effect of Low Temperature.

A number of investigators have tried the effect of subjecting radium to low temperatures, and have obtained negative results in every case. Nevertheless, it seemed worth while to supplement the above experiment by trying the effect of low temperature on the same radium that had been previously heated. Only one temperature was tried, namely, that of liquid air. The quartz tube was hung in a Dewar bulb beside the electroscope and its activity measured. The bulb was then filled with liquid air and measurements taken continuously for an hour, but there was no evidence of any change in the activity.

Conclusions.

The above experiments show no evidence whatever of any change in the activity of the transformation products of radium, when they are subjected to temperatures between $-180°$ and 1600° C. If any change does take place, it is very small, and cannot be over 1 per cent in the case of radium C for temperatures between $-180°$ and 1600°, nor more than 1 per cent in the case of the emanation or radium B for temperatures between $-180°$ and 1500°.

There is thus removed the only known exception to the general rule, that the activity of radio-active substances is not affected by temperature.

In conclusion, I take pleasure in expressing my thanks to Professor Rutherford, who suggested the subject, and furnished all the necessary material for the investigation.

CALCIUM AS AN ABSORBENT OF GASES FOR THE PRODUCTION OF HIGH VACUA AND SPECTROSCOPIC RESEARCH.*

By FREDERICK SODDY, M.A., Lecturer in Physical Chemistry in the University of Glasgow.

(Continued from p. 28).

IX. *Quantity of Argon Detectable by the Spectroscope.*

If air is admitted to heated calcium the oxygen and nitrogen are absorbed almost instantly, and the argon and its companions in the atmosphere remain behind in a state of great purity and freedom from ordinary polyatomic gases. In the apparatus used an arrangement of two taps for admitting known small quantities of gas was joined to the apparatus for the absorption of gases by calcium. The space between the taps was 0·13 cc., and the total volume of the apparatus was 123 cc. The partial pressure of argon is 0·0094 of the atmospheric, or 7·1 mm. Each quantity or "dose" therefore of 0·13 cc. of air admitted to the apparatus corresponds to a pressure of argon of 0·0075 mm. of mercury. The vacuum-tube employed was an ordinary Plücker tube, with aluminium electrodes, of about 4·5 cc. capacity. It was found that no trace of the argon spectrum could be seen in the tube, and no discharge would pass through until three doses of air had been admitted and absorbed. At this stage the group of greens and the orange line in the spectrum were faintly visible. With four doses the red lines were visible momentarily as the nitrogen spectrum faded, and with five doses these became permanent. After ten doses (1·3 cc.) of air had been introduced the whole argon spectrum was brilliant; 4·5 cc. were so added in small quantities and then 3 cc. at once. In one minute the nitrogen spectrum began to clear, and 1·5 minutes the argon reds were visible. In two minutes nitrogen had disappeared, and in under three minutes only argon and hydrogen were visible. The hydrogen disappeared when the heat of the furnace was reduced, and the tube, giving a perfect argon spectrum, was sealed off as a memento of the experiment.

In another experiment the volume of the apparatus was 100 cc., and 12 cc. of air were admitted in one quantity after the calcium had been heated *in vacuo* to the absorbing temperature. This was absorbed without difficulty. The residual argon must have exerted about 1 mm. pressure. Yet the spectrum-tube showed brilliant green fluorescence. A tap was opened and the argon allowed to flow into a similar volume of 100 cc. which had previously been perfectly exhausted. The pressure was thus reduced to about 0·5 mm., and at this stage the spectrum-tube had a resistance equivalent to an alternative spark-gap of 5 mm.

It follows from these experiments that below a pressure of $\frac{1}{5}$ of a millimetre no discharge can be sent through a tube containing argon. At this pressure the greens and orange become faintly visible, and at $\frac{1}{5}$ of a millimetre the reds appear. At 0·5 mm. the resistance of the tube is still so high that the discharge prefers to jump an air gap 5 mm. long, while at a pressure of 1 mm. the tube is brightly fluorescent.

It was found that the substitution for the ordinary vacuum-tube of one of minimal volume with platinum electrodes did not much affect the pressure of gas at which the spectrum became visible. With a tube of 0·3 cc. volume, which is as small as it is convenient to employ, a quantity of argon, less than $\frac{1}{100}$ of a cubic millimetre, measured at normal temperature and pressure, could not be detected by the spectroscope. This applies to the pure gas in the absence of almost every trace of the relatively far more conducting polyatomic gases. As in the case of helium, to be considered, smaller quantities of argon could be detected in presence of hydrogen or other polyatomic gas.

X. *Misapprehensions Regarding High Vacua.*

The foregoing experiments with argon, and others of a similar character with other monatomic gases, serve to show that the characteristics of the electric discharge may prove a very faulty guide to the degree of a vacuum. The terms "X-ray vacuum," "fluorescent vacuum," &c., afford, apart from the knowledge of the character of the residual gas, no indication at all of the actual pressure. For if it happens that the residual gas is a pure monatomic gas, the fluorescent stage, and even the non-conducting stage, are reached at pressures within the range of the mercury barometer. These considerations serve to connect numerous isolated facts familiar to those who have worked with high vacua. Thus it is well known that to pump out a spectrum-tube with a mercury pump takes far less time if the gas pumped out is argon or helium than if air or hydrogen has been present.

[*Added*, Nov. 20.—It is also well known that in vacuum tubes filled with inert gases great heating of the electrodes occurs, even when these are made of aluminium, accompanied with the rapid disintegration of the electrode and the volatilisation of the aluminium (compare, for example, E. C. C. Baly, *Phil. Trans.*, 1903, A, vol. ccii., p. 183). At the same time a rapid exhaustion of the supply of gas apparently takes place, the vacuum appears to rise, the tube rapidly becomes fluorescent with use, and the resistance increases to the non-conducting point at which no discharge can be passed through the tube. In the past this has been attributed to the absorption of the gas by the

* Read before the Royal Society, November 15th, 1906

electrodes and the walls on which the volatilised aluminium is deposited. The advantages of aluminium over other metals, such as platinum, has been ascribed to a more rapid absorption in the case of the heavier metals (compare Travers, "Study of Gases," p. 299). Attempts to recover the gas supposed to be absorbed by heating the apparatus, solution of the metal electrodes, &c., have not been successful, as only a trace of the gas is recovered in this way.

The true explanation of the phenomenon is quite different, and follows simply from the experiments given in Section IX. for argon, and similar ones in Sections XI. and XII. for helium. The inert gases are not absorbed, but remain in undiminished quantity in the gaseous state in the tube, but the traces of ordinary chemically active gases always present initially or introduced from the electrodes during the discharge are absorbed, and the tube becomes in consequence non-conducting. The experiments of Skinner have an important bearing on this question, and in his most recent paper he summarises his conclusions (*Phil. Mag.*, November, 1906, p. 481). When a current is passed through a vacuum-tube, entirely independently of the nature or amount of gas filling the tube, hydrogen is evolved from the cathode and absorbed by the anode at a rate initially equal to that required by Faraday's law. Aluminium and magnesium cathodes give out hydrogen much more freely than the denser metals, but the rate of *evolution* from the cathode rapidly falls off as the supply of gas in the surface layers of the metal is exhausted. If the tube is allowed a rest the initial rate is recovered. When a continuous discharge is passed through any tube, therefore, the vacuum improves, for the rate of absorption by the anode gains on the rate of evolution from the cathode; and this should suffice to explain the well-known improvement with use in the vacuum of an X-ray tube. According to Skinner helium and argon are *not* absorbed by the electrodes, hence the rapid exhaustion or "running out" of the tube, and the advantages of the aluminium electrode are to be explained only in the manner indicated. It is intended to try, by passing a unidirectional current through a tube filled with inert gas, to what gas-pressure the non-conducting stage can be pushed. It is not a little remarkable, from the theoretical point of view, that helium, which conducts so much more readily than any other gas under usual conditions at high pressure, should exhibit the peculiar behaviour it does at low pressure in a state of purity.

Frequently in the work on the production of helium from radium, in conjunction with Sir William Ramsay, it was noticed when "running" a spectrum-tube to absorb nitrogen and reveal helium, if present, that, although a severe and prolonged running might be necessary to absorb the nitrogen, it always "ran out" first, and helium, however minute in quantity, showed itself, if present, as the nitrogen spectrum faded. When, however, the nitrogen spectrum had completely faded, which it did usually with great rapidity once it commenced to weaken visibly, the helium "ran out" almost instantly, if only in minute quantity, and the tube refused to conduct the discharge. This sharp preferential absorption, as it seemed, of the nitrogen first by the electrodes, so that even after a quarter of an hour's hard running the helium would survive, instantly to disappear as soon as the nitrogen faded, always seemed to me almost providential, until, recently, the true explanation became obvious.]

The explanation is also to hand why the presence of mercury vapour affects the action of the mercury pump so little. The vapour pressure of mercury at room temperature is between 1/500 and 1/1000 of a millimetre. In the case of hydrogen or carbon dioxide it is probable that this pressure would be sufficient to conduct the discharge and prevent the vacuum appearing very high to the electrical test. That "high vacua" can be obtained at all by the mercury pump is probably due to the fact that mercury vapour is monatomic.

Similar considerations apply to the vacua so readily and simply obtained by the use of charcoal cooled in liquid air, according to the method now largely used in scientific investigation and first employed by Sir James Dewar (*Proc. Roy. Soc.*, 1904, A, vol. lxxiv., pp. 122—131). It happens here also, as in the case of the calcium method, that the unabsorbed gases are monatomic. At liquid air temperature the helium and neon in the air remain very largely unabsorbed by charcoal. Sir W. Ramsay has determined in this way the proportion of these gases in the atmosphere, and found 17 parts per million of the two gases together (*Proc. Roy. Soc.*, 1905, A, vol. lxxvi., p. 111). An earlier determination made by Dewar, without the use of charcoal, was identical with this (*Proc. Roy. Inst.*, 1902, vol. xvii., pp. 223—230). The figures obtained by Ramsay, however, are for the total gases left uncondensed by charcoal at liquid air temperature, and have a direct bearing on the present question. Now as Lord Blythswood and Allen have shown (*Phil. Mag.*, October, 1905, p. 497), there is no difficulty in exhausting an X-ray bulb by the use of cooled charcoal from atmospheric pressure to the point at which it is difficult to force a discharge through the bulb. Yet the pressure of the helium and neon in the bulb must be 17 millionths of the initial pressure, or about $\frac{1}{5}$ of a millimetre. This result, although appearing strange by itself, is consistent with the experiment on the pressure of argon necessary to allow the discharge to pass. When any method of measuring the amount of gas remaining in the exhausted space, other than the electrical, is employed, the deficiencies of the non-conducting vacuum produced by cooled charcoal, when the vessel was originally filled with air at atmospheric pressure, become at once apparent. If, for example, the degree of vacuum obtained is measured by the rate of evaporation of liquid air in a Dewar flask, then the presence of these residual monatomic gases becomes all important. Experiments of a quantitative character on this subject are being made by Mr. Berry in this laboratory. (See addendum to this paper, *prox.*)

[*Added*, Nov. 20.—Lord Blythswood and H. S. Allen (*loc. cit.*), after showing, in the first part of their paper, that an X-ray bulb could be exhausted by cooled charcoal from atmospheric pressure in one hour to "a vacuum so good that the tube had to be heated in order to allow the discharge to pass through it," describe in the second part experiments in which the final pressures realised were measured by means of a McLeod gauge. When the apparatus was exhausted by a Fleuss pump initially to 40 mm., the final pressure attained was 0·0009 mm., whereas, starting from a pressure nearly atmospheric, the final pressure attained was ten times as great. They point out the importance of the preliminary exhaustion when an extremely high vacuum is required, owing to the presence of the less easily condensible gases, hydrogen, helium, and neon in the air, but do not refer to the apparent inconsistency between the results with the McLeod gauge and their earlier ones with the electric discharge test.

I was present at the meeting of the Philosophical Society of Glasgow (March 22, 1906), when Mr. Allen showed experimentally the exhaustion of an X-ray bulb from atmospheric pressure by cooled charcoal, and I was much impressed at the time with the apparent inconsistency between this result and the recent measurements of Sir W. Ramsay already cited.

The allusions in this section to the results of use of the charcoal method have reference solely to the phenomenon of the bad conducting quality of the residual inert gases that remain when air is absorbed from atmospheric pressure by use of charcoal or other methods. The question of the degree of vacuum produced under proper conditions for obtaining the best results is, of course, entirely different. Although the test of non-conductance, which has, so far, been relied upon implicitly for gauging the goodness of the vacuum, is useless, and may be actively misleading in the case of vacua obtained by the use of cooled charcoal without preliminary exhaustion by a pump (compare also G. Claude and Rene J. Levy, *Comptes Rendus*, 1906, vol. cxliii., p. 876), there is no doubt at all that, with suit-

able procedure, this method can give a very high degree of exhaustion. (*Cf.* the experiments described by Mr. Berry in the addendum to this paper).

XI. *Quantity of Pure Helium Detectable by the Spectroscope.*

Mixtures of known composition were made of helium and oxygen, and known quantities introduced into the calcium absorbing apparatus of known volume. The pressure of the residual helium could thus be calculated. In one case 0·13 cc. of helium was made up to 104 cc. with oxygen, so that the mixture contained $\frac{1}{8}$ per cent of helium. Successive quantities, each of 0·13 cc., were introduced into the apparatus, the volume of which was 89 cc., including an ordinary Plücker tube of volume 4·5 cc. The following observations are extracted from the note-book. The "quantities" referred to are each 0·13 cc. of the mixture, and the test of non-conductance was an alternative spark-gap of 2·5 cm. in air.

1st quantity.—Glimpse of D_3 for a fraction of a second as the oxygen spectrum suddenly cleared and tube became non-conducting.

2nd quantity.—D_3 clear while the tube conducted, which was but momentarily.

3rd quantity.—D_3 very pure and distinct, but tube became non-conducting.

5th quantity.—D_3 at first brighter than the mercury yellows.

6th quantity.—D_3 the brightest line at first except for the oxygen orange-red line.

7th quantity.—Just before the non-conducting point the general spectrum was plainly recognisable as helium.

8th quantity.—The brighter helium red (6677) visible.

9th quantity.—The two blues and violet seen.

10th quantity.—First glimpse of the peacock-green line (5016).

Tube took four minutes before it became non-conducting.

11th quantity.—Eight minutes before non-conductance.

13th quantity.—The helium spectrum was now quite good while it lasted, but the tube became non-conducting in three minutes.

The experiment was continued without much alteration up to the point at which thirty-five quantities had been added. The helium spectrum was plain, and indeed brilliant, so long as the tube conducted, but always a point was reached at which the discharge refused to pass. Diffusion was hastened by alternately heating and cooling the furnace. At the 35th quantity the tube conducted one way of the commutator and not the other, and this was taken as the limiting value. Later in the day and next morning the tube showed the same result. The discharge just passed, but the spectrum was feeble. The line D_3 was clear and the peacock-green exceedingly faint. These were the only helium lines visible.

The pressure of helium corresponding to each dose is 0·0014 mm., and to thirty-five doses 0·049 mm. It is thus clear that pure helium at a pressure of less than $\frac{1}{20}$ mm. is non-conducting to the discharge, while far less than this can be detected in presence of other gases. Like mercury vapour and krypton, a very small trace is visible in the spectrum of another gas. In the above experiments the D_3 line was visible plainly when only a single dose was added, so that to get the minimum quantity detectable a fresh series of experiments with more dilute mixtures was necessary.

XII. *Most Favourable Conditions for the Detection of Infinitesimal Quantities of Helium.*

Collie states that in presence of large quantities of mercury vapour the blue helium line, 4922, is the most delicate test for helium, and can easily be seen when none of the other helium lines are visible (*Proc. Roy. Soc.*, 1901, vol. xlxxxi., p. 25). It is likely, however, that the author mistook for helium a line in the spectrum of mercury which has the wave-length 4916·4 (Stark), and which is prominent in the mercury vapour-lamp spectrum. It is not often seen in the Plücker tube, except when the latter is warm and liquid mercury is present, so that the vapour pressure of the mercury is considerable. Collie has suggested for the calibration of spectroscopes a tube containing liquid mercury, helium, and hydrogen, as the spectrum consists of a large number of standard lines fairly equally distributed throughout the length of the spectrum. In such a tube I kept the blue line in question under close observation in a good spectroscope. With a feeble discharge, the tube cold and the mercury spectrum faint, this line was single and due to helium only. As the strength of the discharge was increased and the tube warmed, the mercury spectrum intensified, and a second line became visible on the more refrangible side of the helium line, and distant from it roughly about as far as D_3 is distant from D_2. On still further increasing the strength of discharge the helium line disappeared entirely, and the line was again single and due to mercury only. On diminishing the discharge and allowing the mercury vapour to re-condense, the less refrangible line reappeared and grew in strength as the other faded, and finally alone remained visible. Thus, it is clear that so far from enhancing the strength of the helium line, 4922, the presence of mercury serves to mask it completely even in presence of considerable quantities of helium. This line, 4916, is seen equally well in a tube containing mercury in which no helium has been introduced. Under no conditions tried has the line 4922 been seen when D_3 was invisible. The latter is by far the most delicate test for the presence of helium, and becomes visible with a quantity many times less than suffices to develop any other line in the spectrum.

Some experiments with various kinds and sizes of spectrum-tube, some with aluminium and others with platinum electrodes, showed that with minimal quantities of helium at similar *pressure* it is slightly easier to detect the D_3 line in the ordinary Plücker tube of volume 4·5 cc. than in a tube of minimum volume. But the difference is not great, and is mainly due to the sodium lines from the glass being more prominent in a tiny tube masking the D_3 line. Certainly, when the object is to detect the smallest possible *quantity* of helium, the tube should be of as small volume as possible. A series of experiments was tried in which the quantities of helium, far smaller than those necessary to allow the discharge to pass when in the pure state, were examined in presence of hydrogen and oxygen. A mixture containing 0·015 per cent of helium with oxygen was prepared by the principle of successive dilutions. Known quantities were introduced into the calcium absorption apparatus of known volume. After the oxygen had been completely absorbed, connection between the spectrum-tube and the absorption chamber was closed, and traces of oxygen and hydrogen introduced into the gas in the spectrum-tube. This was accomplished by heating a trace of solid potash, previously fused and freed from water, *in vacuo*, or by momentarily raising to redness a spiral of platinum wire by means of a current. It does not appear to make much difference which gas is added to conduct the discharge. After the first momentary heating platinum gives oxygen free from hydrogen. The potash gives hydrogen, doubtless as water vapour. The function of this gas is merely to cause the discharge to pass. Once established a large part, perhaps the larger part, of the current is carried by the helium, the spectrum of which, under these conditions, appears with extraordinarily minute quantities.

With an ordinary Plücker tube and an apparatus of volume 111 cc. after three doses, each of 0·13 cc. of the 0·015 per cent mixture, D_3 was but momentarily visible, and could not be again brought out by introducing oxygen or hydrogen. With four doses D_3 was faint but clear and permanent, and this may be taken as the extreme limit of visibility. The partial pressure, due to the helium at this stage, is only 1/100 of that necessary to conduct the discharge when pure, being 0·0005 mm. as compared with

0·05 mm. for the case of the pure gas discussed in the last section.

(The point was raised in the discussion of the paper, how far it had been actually proved that the inert gases were not absorbed, at least in part, by the walls and electrodes. The last experiment answers this question, for in a tube containing only one-hundredth of the quantity of helium necessary to conduct the discharge in the pure state, the helium spectrum may be brought out afresh by introducing a minute quantity of hydrogen or oxygen, which would not have been the case if the helium had been absorbed when the tube became non-conducting).

If a vacuum-tube of 0·3 cc. volume is used, it follows that a quantity of helium, 1/4000000 part of a cc., measured at normal temperature and pressure, would be within the range of detection by the spectroscope. For safety a margin of twice this quantity should be allowed, or 1/2000 of a cubic millimetre. This quantity weighs 10^{-10} grms., and contains about 2×10^{18} atoms. The delicacy of the test may be indicated by the following consideration:—It can be calculated on the assumption that the α-particle is an atom of helium, that a kilogrm. of uranium nitrate would generate 1 cc. of helium in a period of about 5000 years. The amount of helium produced in a single day should be within the range of spectroscopic detection. Researches on the production of helium from uranium and thorium have been in progress for some time, and it is hoped, now that the ground is cleared, that the matter would soon be put to a definite quantitative test.

In the above experiments the actual quantity of helium used was, of course, many times the amount finally examined in the spectrum tube. It is easy, however, to fill the absorption chamber after cooling completely with mercury, and to compress the gas into the spectrum tube. In this operation the minute quantity of hydrogen left unabsorbed by the calcium is, after the compression, just of the right amount to conduct the discharge and to reveal any trace of helium without any additional arrangement.

As an example of an actual experiment, one may be taken from the note-book from an examination of the gases present in native platinum. On the view that the scarcity of an element, after prolonged and extensive search for it, justifies the suspicion that it may be a member of a disintegration series, it was thought possible that evidence of such disintegration might appear in the presence of rare gases in platinum, as is the case with the radio-active minerals. Messrs. Johnson and Matthey very kindly lent me as much native platinum as required, and I desire to acknowledge my indebtedness to them for their kindness.

In one experiment a quantity of about 300 grms. was heated in a porcelain tube in an electric oven to 1200° C., and the gases passed into a calcium absorption chamber of the usual kind provided with a tiny spectrum tube at the upper end. A trace of carbon dioxide, from the walls probably, first came off. Then nitrogen appeared, and, as the temperature approached 800° C., carbon dioxide in quantity. On closing the connection with the platinum and absorbing the gas with calcium, the spectrum tube became quite non-conducting. These operations were repeated, the gas evolved being admitted and absorbed in stages. When the electric oven had reached a temperature of 1000° C. a momentary glimpse of the D_3 line was seen. At 1100° C. the peacock-green line was picked up, and the more prominent of the two reds seen extremely faintly. On forcing the discharge the argon greens could be faintly made out in a Ramsay pocket spectroscope. When the oven reached 1200° C., a large quantity of carbon dioxide had accumulated. This was admitted to the absorption chamber, and the connection sealed, and the heating of the platinum stopped. On cooling the calcium after absorbing the gases, the spectrum-tube was on the verge of non-conductance, but extremely faint helium could be detected. Mercury was admitted, and the contents compressed completely into the tiny spectrum tube. The helium spectrum was now reasonably bright, all the lines being visible, together with the hydrogen red and the mercury lines. With the pocket spectroscope argon could just be detected. It was estimated from the appearance of the discharge at various stages of the compression that about one-fifth of a cubic millimetre of helium was present, a quantity 400 times as much as could have been detected, yet only representing 1/15000000 per cent by weight of the platinum. The experiment lasted but two hours, and is given merely as an example of the ease with which an infinitesimal quantity of helium may be separated from large amounts of other gases by means of calcium, and its quantity estimated with fair probability. No weight is to be put on the result as indicating the origin of the helium. As a matter of fact, the native platinum was quite distinctly though feebly radio-active, 300 grms. of it in an electroscope producing an effect equivalent to 0·07 mgrm. of uranium oxide. Cleveite usually contains about 2 cc. of helium per grm., and is usually of about the same activity as uranium oxide. The platinum contained about 3,000,000 times less helium, and was about 4,000,000 times less radio-active than cleveite, so that there is no reason to go further to explain the source of the helium than to suppose that a trace of some radio-element is present in native platinum.

(To be continued).

NOTICES OF BOOKS.

Notes on Qualitative Analysis. By H. J. H. Fenton, Sc.D., &c. New Edition, Revised. Cambridge: The University Press. 1906.

When this book was first published it was very well received, for it gave a complete course of qualitative analysis according to the usual schemes, while at the same time treating the subject far more fully than was then customary in an elementary book, and devoting more space to explanations and discussions of the various reactions. Although the time when practical chemistry from a school point of view meant nothing more than a course, generally imperfectly understood, of qualitative analysis, has now passed, let us hope for ever, the value of systematic analysis as a training is recognised on all sides, and teachers cannot do better than put this book into the hands of their pupils. The author in preparing the new edition has added many fresh methods and tests, and has increased the number of organic substances treated. A scheme is included for the identification of the common gases, and the classification of oxides is also briefly discussed. The theoretical explanations have been subjected to a careful revision, and the table of the examination of a substance for one acid radicle, which in the earlier editions required considerable amplification, has now been much enlarged and improved.

Producer Gas. By J. Emerson Dowson, M.Inst.C.E., M.Inst.M.E., and A. T. Larter, B.Sc. (London), F.C.S. London, New York, and Bombay: Longmans, Green, and Co. 1906.

The authors of this monograph write as enthusiastic believers in the great future which lies before producer gas, and as the book is practically the first of its scope it should be cordially welcomed by engineers, who will find it a valuable work in many respects. The subject is first treated from the theoretical point of view, and then the practical applications of the gas are classified and discussed, certain branches being treated comparatively fully; for instance, two chapters are devoted to the suction type of plant. The illustrations with which the book is provided are in most cases very diagrammatic, but they have the merit of being clear and easily understood. Interesting and lengthy accounts of the various tests which have been made with different types of plant are given, and the

chapter on the comparison of steam and gas power, in which the heat efficiency of a gas plant and gas-engine is considered and compared with that of a boiler and steam-engine of the same power, contains some striking figures and graphic representations.

The Scientists' Pocket-book and Diary. Manchester: James Woolley, Son, and Co., Ltd. 1907.

"The Scientists' Pocket-book and Diary" for 1907 contains a large amount of useful information, which has been judiciously selected. A particularly noticeable table is that which gives the properties and sources of the rare elements, and the most important physical constants of all the solid elements have also been tabulated. The little book is issued at a very modest price, and the statistics, as far as we have been able to test them, appear to be accurate.

Ice Formation. By Howard T. Barnes, M.A.Sc., D.Sc., F.R.S.C. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1906.

The practical importance of a thorough knowledge of ice phenomena to hydraulic engineers in Canada is immense, and the Associate Professor of Physics at the McGill University has rendered a public service to his countrymen in producing this admirable exposition of the subject. He bases his discussion of the formation of frazil and anchor ice, to which special reference is made, upon the study of the physical laws governing the transfer of heat, which he deals with in the first chapter, passing thence to the physical constants of ice and their determination. Recent work is carefully reviewed, and experimental details are fully described, while the later chapters on the formation and structure of ice are particularly interesting. Much of it, illustrated as it is by good photographs, will appeal to a wide public, and the extract from the Report of the Montreal Flood Commission gives the reader a very clear conception of the conditions which hold in the region of the St. Lawrence River. The description of the author's own experiments on the determination of the temperature of the waters of the river during the winter is preceded by a chapter on the measurement of temperature by refined methods, with special reference to the work of Prof. Callendar; the discussion of theories to account for the formation of anchor ice displays a somewhat marked partisan spirit, but also shows evidence of the author's originality and fertility of ideas. Although the book will naturally be more widely circulated in Canada than here, the author's extensive experimental work entitles him to the attention of scientific men of all nations, and his book gives a complete account of the phenomena of ice formation, collecting much scattered information and welding it into an interesting and valuable whole.

Outlines of Qualitative Chemical Analysis. By Frank Austin Gooch and Philip Embury Browning. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1906.

Although the authors of this book have some useful suggestions to make regarding the adoption of a few new tests and methods of separation, this fact hardly seems to warrant the production of a new book, in other respects very ordinary, on qualitative analysis, and there appears to be no real need to add to the number of books on routine work, which has been treated in many excellent and trustworthy text-books. However, this book has its good points. The introduction on procedure and principles is both interesting and clear, and is exactly what is wanted, being full enough and yet sufficiently condensed to give the lazy or hurried no pretext for skipping those theoretical considerations which are of the utmost importance and yet are frequently neglected. In minor details there is much to criticise unfavourably, and also a good deal to praise. To take the last first, the scheme of preliminary analysis is full and clear, and should give the student great assistance in the identification of unknown substances. The organic substances chosen for consideration are well selected, and the use of organic reagents in the separations (amyl alcohol, for example, to separate strontium and calcium) is sensible, and has many advantages. On the other hand, it ought to be recognised that some indications of the strengths of the reagents employed are essential to enable the student to work intelligently, and the scheme for acidic analysis is not as clear as it might be, while the value of the solubility table would be greatly increased if it gave the number of grammes dissolved per cubic centimetre in a saturated solution, instead of merely comparative information.

The Science Year-book, 1907. London: King, Sell, and Olding, Ltd.

Very few alterations have been made in the 1907 issue of this Year-book, which combines in one volume a diary, directory of scientific societies, and collection of biographical notices, besides containing many tables, astronomical, physical, and chemical. Special prominence is given to astronomical information, but practically all branches of science are represented, and the tables are very well arranged. The summaries of progress which were divided under different headings last year have now been condensed into one general article dealing shortly but adequately with the advancements and developments of the year 1906. For those who do not wish for the diary portion an abridged edition is issued; this contains all the matter of the Year-book without the Diary, and is naturally published at a lower price.

Post's Chemisch-Technische Analyse. ("Post's Technical Analytical Chemistry"). Edited by Dr. Bernhard Neumann. Third Edition. Braunschweig: Friedrich Vieweg und Sohn. 1906.

The new edition of this work contains much fresh matter relating to improved tests and processes, but the compiler's policy of rigorously excluding all unnecessary or out-of-date matter has enabled them to keep the book from becoming unwieldy, although it comprises a complete collection of the best methods of testing all technical products. The work is equally suitable for use in technical schools and colleges, and in works' laboratories, and every effort has been made to include only those processes which may be relied upon to give the most accurate results, and which are convenient in practice. It is issued in two volumes, each of which appears in four parts, dealing as far as possible with groups of allied industries, and the fact that each chapter has been written by a well-known specialist is a guarantee of trustworthiness. The book has been completely revised for the preparation of the third edition.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 1, January 7, 1907.

The Distillation of Alloys of Silver and Copper, of Silver and Tin, of Silver and Lead.—Henri Moissan and Tosio Watanabe.—By a series of distillation experiments, M. Moissan has already found the conditions of vaporisation of certain metals and their properties when condensed on a cold surface. The authors have attempted to verify these results by investigating the distillation in the electric furnace of a certain number of alloys. Volatile

metals were chosen for the purpose, the alloys containing one in common, viz., silver, so as to give comparable results. The time of heating was varied from one to fifteen minutes, the current being kept as constant as possible. 1. *Alloy of Silver and Copper.*—Results showed that the longer the distillation continued the richer the alloy became in copper, thus proving the boiling-point of copper to be higher than that of silver; the original alloy containing 49·55 per cent silver and 49·65 per cent copper, which after fifteen minutes' heating became 3·62 per cent silver and 95·22 per cent copper. 2. *Alloy of Silver and Tin.*—The original alloy contained 36·98 per cent silver and 64·04 per cent tin; after ten minutes' heating the composition changed to 2·93 per cent silver and 93·65 per cent tin, showing that the boiling-point of tin is higher than that of silver. 3. *Alloy of Silver and Lead.*—The alloy at the beginning contained 46·24 per cent silver and 52·95 per cent lead; after heating for two and a-half minutes, analysis showed the quantity of silver to be 93·81 per cent silver; hence lead distils more rapidly than silver. *Conclusions.*—These experiments, though performed in equal time intervals with all other conditions constant (ampèrage, voltage, diameter of electrodes, capacity of furnace), are not entirely comparable, because the amount of heat supplied by the arc in a cold apparatus or in an apparatus raised to 2000° is not the same for equal intervals of time. Hence, the results obtained are only approximate, but they serve to indicate that the four metals, according to their boiling-point, may be classed in the following order:—Lead, silver, copper, tin.

Alkaline Reduction of the Para- and Meta-Nitrobenzophenone.—P. Carré.—The author undertook the reduction of these two bodies by means of alcoholic soda and zinc, in order to ascertain the possibility of obtaining the corresponding azo-derivatives without alteration of the ketonic function. He, however, found this was not possible. Paranitrobenzophenone furnishes upon reduction a mixture of *p*-azo- and of *p*-azoxybenzophenone, and metanitrobenzophenone furnishes *m*-azoxybenzophenone with breaking down of the molecule in both cases.

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Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 16, 1906.

Compounds of Pentavalent Chromium.—R. F. Weinland and M. Fiederer.—The authors have found that chromium oxychloride can combine with the chlorides of the alkali metals, forming double salts which contain one molecule of chromium oxychloride to two of the alkali chloride, and no water of crystallisation. They are formed by dissolving chromic acid in water, adding hydrochloric acid cooled to $-20°$, and saturated with hydrochloric acid gas, and adding a strong solution of the alkali chloride to the oily chromium oxychloride which separates out, and leading in hydrochloric acid gas. The rubidium and cæsium salts form regular octahedra, and the potassium salt crystallises in the rhombic system. They behave very similarly to the corresponding pyridine and quinoline compounds. They are stable in dry air, but rapidly decompose in damp air. The aqueous solution gives with ammonia a precipitate of chromium hydroxide, and with lead acetate a precipitate of lead chromate. The pentavalency of chromium in the new double salts is proved by the fact that isomorphic mixtures of the cæsium salt with the analogous compound of niobium oxychloride can be prepared, and the niobium in the oxychloride is undoubtedly pentavalent.

Influence of the Chemical Constitution of Nitrogenous Food upon the Fermentive Power of Yeast.—Hans Pringsheim.—The author's experiments show that yeast grown in absence of sugar is capable of inducing fermentation if supplied with nitrogen in a suitable form. Thus after a growth of three months on a litre of malic or succinic acid with leucin as source of nitrogen the liquid is separated from the sediment of yeast, and sugar is added to the small amount of liquid remaining with the yeast; after twenty-four hours an appreciable development of gas occurs, and a loss of carbon dioxide is detected, amounting to 0·22 grm. with malic acid and 0·20 grm. with succinic acid. It has also been shown by the author that yeast can only cause the sugar given to it to ferment if the source of nitrogen contains the group .NH.CH.CO, while all other sources which do not possess this group cannot induce the formation of a fermentable plasma.

Determination of Halogens in Organic Compounds by means of Metallic Sodium and Ethyl Alcohol.—A. Stepanow.—The weighed substance, *e.g.*, monochlorbenzene, is put in an Erlenmeyer flask with 20 to 40 cc. of ethyl alcohol (98 per cent). The flask is connected with a long upright condenser, and put on a water-bath, and metallic sodium is then introduced through the condenser in large excess, the quantity being twenty times that required according to the equation—

$$R.Hlg + C_2H_5.OH + Na_2 = R.H + NaHlg + C_2H_5.ONa.$$

After the sodium has dissolved the contents of the flask are diluted with 20 to 40 cc. of water, and the alcohol is distilled off. Then dilute nitric acid is added to the cold liquid till its reaction is strongly acid, and the halogen is titrated by Volhard's method. This way of determining halogens is simple and quick, while the results obtained are very accurate.

Action of Phosphorus Pentabromide or Pentachloride on Phenol Alkyl Ethers.—W. Autenrieth and Paul Mühlinghaus.—When phosphorus pentachloride acts at a high temperature on alkyl ethers the following reaction occurs:—

$$CH_3.CH(OC_2H_5)_2 + PCl_5 = CH_3.CHCl.OC_2H_5 + POCl_3 + C_2H_5.Cl.$$

Hence it might be supposed that when phenol alkyl ethers were substituted the corresponding reaction, $Ph.O.R + PCl_5 = Ph.Cl + POCl_3 + RCl$, would occur. This, however, is not the case. When either PBr_5 or PCl_5 acts upon phenol alkyl ether, either in the cold or on gently warming, an energetic reaction occurs, and large volumes of hydrogen haloid are evolved, while phosphorus tribromide or trichloride and phenol ethers brominated or chlorinated in the benzene ring are formed. The reaction is represented by the equation—

$$C_6H_5.O.R + PBr_5 = C_6H_4Br.O.R + PBr_3 + HBr.$$

Naphthol ether reacts exceedingly easily, and all the reactions occur at temperatures considerably below the dissociation temperatures of phosphorus tribromide or trichloride. Substituted phenol ethers behave similarly, but in many cases it is necessary to heat for a long time on the water-bath. The general method adopted by the authors was as follows:—The phenol ether was placed in a dry flask with calcium chloride, and the thoroughly dried phosphorus pentabromide was added in small quantities, the whole being well shaken between each addition; then the mixture was heated for a short time (about ten to fifteen minutes) until the phosphorus haloid was dissolved, and the vigorous evolution of hydrogen haloid had nearly ceased. In most cases a reddish or brown coloured liquid was thus obtained. This was thoroughly shaken with large quantities of cold water when the brominated or chlorinated phenol alkyl ether separated, and could be shaken up with ether, and purified by fractional distillation or re-crystallisation. The yield amounted to 90 per cent or more of the theoretical yield.

Alteration in the Colours of Substances of Unalterable Constitution.—A. Hantzsch and W. H. Glover.—In the case of those coloured substances (mostly of the nature of salts) which are formed from colourless compounds by intramolecular transposition, and are either electrolytes or can yield electrolytes, by apparently simple substitutions, *e.g.*, of hydrogen by metals, the colour can be suddenly changed; it appears or disappears discontinuously, as in indicators. On the other hand, in the case of the coloured organic non-electrolytes, *e.g.*, azo bodies,

quinones, coloured diketones, &c., the colour can be continuously increased or diminished without intramolecular transpositions according to the nature of the groups combined with the chromophore molecules. These phenomena are well known, but have not been investigated quantitatively, partly because the accuracy of colorimetric experiments generally leaves much to be desired. The authors have examined the colour and colour intensity of various "indifferent" organic compounds with reference to their alteration by chemically indifferent substituents and by the influence of different solvents. They used König's spectral photometer, as modified by Martens and Grünbaum, and obtained concordant results with it. The substances investigated included bis-diphenylene ethylene, azobenzene and its derivatives, also quinones and quinone dioximes. As solvents absolute alcohol, ether, chloroform, benzene, ligroin, and hexane were used, as well as glacial acetic acid, acetone, and sometimes caustic soda. The results obtained may be collected as follows:—1. Beer's Law (that the colour intensity of a dissolved substance is directly proportional to its concentration) holds good for solutions of coloured non-electrolytes within all concentration limits (up to exceedingly great dilution). The deviations from the law observed in the case of electrolytes, and more especially coloured salts, are to be ascribed to chemical causes (hydrolysis, &c.). 2. The colour intensity of solutions of coloured non-electrolytes is dependent upon the nature of the solvent. Solvents containing oxygen, for example, water and alcohol, produce brighter colours than hycrocarbons, especially benzene. 3. The oxyazo-substances which produce salts (especially the quinone dioximes) give rise to intensely coloured alkali salts. The formation of salt must be accompanied by a chemical change, hence these substances are pseudo-acids. 4. By alkylating and acylating *p*-oxyazobenzene, and toluene azophenol, the colour is deepened, independently of the nature of the substituent, but almost proportionally to its molecular weight.

Triphenylmethyl and Trivalent Carbon.—Julius Schmidlin.—The magnesium compound of triphenylchlormethane occurs in two forms, one of which is decomposed by dilute hydrochloric acid giving triphenylmethane, while the other yields triphenylmethyl. When magnesium acts on triphenylchlormethane in ethereal solution, the magnesium compound of the triphenylmethyl type first results (the α-form). By heating this the stable *β*-form is obtained. The two substances are isomeric, and the formula of the *β*-substance is undoubtedly $(C_6H_5)_3C.MgCl$, and as triphenylmethyl can be obtained only from the α-form which does not contain the group $(C_6H_5)_3C$, triphenylmethyl itself cannot be $(C_6H_5)_3C$. The author has prepared the two magnesium compounds, and compared their properties, and has proved that there is no triphenylmethyl in the solution of the α-magnesium body, for, firstly, the peroxide formed by leading oxygen into the original solution of the magnesium compound arises, not from the previously formed triphenylmethyl, but directly from the magnesium compound, and, secondly, the triphenylmethyl resulting from the decomposition of the α-compound actually results at the moment of decomposition, and was not present in the solution previously.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, January 29, at 3 o'clock, Professor A. C. Seward commences a course of two lectures at the Royal Institution on "Survivals from the Past in the Plant World"; on Thursday, January 31, at the same hour, Major P. A. MacMahon delivers the first of two lectures on "Standards of Weights and Measures"; and on Saturday, February 2, the Rev. W. Barry begins a course of two lectures on "Papal Deposing Power." The Friday Evening Discourse on February 1 will be delivered by Sir Almroth E. Wright on "The Methods of Combating the Bacteria of Disease in the Interior of the Organism," and on February 8 by Professor J. Gollancz on "Old English Poetry."

Appointment.—Professor G. P. Darnell Smith, B.Sc., F.I.C., F.C.S., has been appointed Assistant Director of Technical Education and Manual Training to the Board of Education, Auckland, New Zealand. Mr. Darnell Smith has been on the staff of the Merchant Venturers' Technical College, Bristol, since September, 1892; some time ago he was promoted to the post of Assistant Professor of Chemistry in the College.

MEETINGS FOR THE WEEK.

MONDAY, 28th.—Society of Arts, 8. (Cantor Lectures). "Gold Mining and Gold Production," by J. W. Gregory.

TUESDAY, 29th.—Royal Institution, 3. "Survivals from the Past in the Plant World," by Prof. A. C. Seward, F.R.S.

—— Society of Arts, 8. "The Artistic Treatment of the Exterior of the Pianoforte," by Wm. Dale.

—— Faraday Society, 8. General Discussion on Osmotic Pressure. The Earl of Berkeley will exhibit and describe his Apparatus for the Direct Measurement of Osmotic Pressure. Mr. W. C. Dampier Whetham, F.R.S., will speak on "Indirect Methods of Measuring Osmotic Pressure." "Dr. T. M. Lowry will speak on "Osmotic Pressure from the Standpoint of the Kinetic Theory."

WEDNESDAY, 30th.—Society of Arts, 8. "Apprenticeship," by James Parsons, M.A.

THURSDAY, 31st.—Royal Institution, 3. "Standards of Weights and Measures," by Major Percy A. Macmahon, F.R.S.

FRIDAY, Feb. 1st.—Royal Institution, 9. "The Methods of Combating the Bacteria of Disease in the Interior of the Organism." by Sir Almroth E. Wright, F.R.S., &c.

SATURDAY, 2nd.—Royal Institution, 3. "Papal Deposiog Power," by the Rev. William Barry, D.D.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2462.

VOLUMETRIC ESTIMATION OF ANTIMONY.

By J. B. DUNCAN, B.Sc.

About three years ago there appeared in the *Chemiker Zeitung* an article by Nissenson and Siedler on the volumetric estimation of antimony in hard lead by means of potassium bromate. The method was immediately tried by me in the laboratory of Messrs. Cookson and Co., Ltd., antimony smelters, where a number of accurate assays are required daily. It gave very good results. An attempt was then made to apply the method to ores and slags, and to diminish the time taken for an assay. After many trials the following modifications were found to give good results. They are rapid and equally applicable to alloys and ores, and have been in constant use ever since.

A solution of potassium bromate is prepared by dissolving 2·7852 grms. in a litre of water and standardised by the following process:—Weigh out 0·3 grm. of pure finely divided antimony metal. Place in a 16 oz. beaker, cover, and add 20 cc. of strong hydrochloric acid and a few drops of bromine. Keep warm, with occasional shaking, until the metal is dissolved. Boil off the excess of bromine, cool a little, and then add about 0·75 grm. of sodium sulphite, and boil the mixture down to about half its volume to drive off sulphur dioxide. (In the case of alloys this latter operation will also remove any arsenic present). Rinse the cover and sides of beaker with hot water, and add a little hydrochloric acid. The liquid is then heated to boiling, and the bromate added from a burette until nearly all the antimony has been oxidised. Three drops of methyl-orange solution are now added, and the bromate run in until the colour of the methyl-orange is destroyed. The number of cc. of bromate used is equivalent to 0·3 grm. of antimony. A duplicate assay is made. The amount of bromate required in each case should be the same, and will approximately be 50 cc. Thus, 1 cc. of the bromate is equivalent to about 0·006 grm. antimony. The standardisation of the bromate may also be made on antimony oxide, or an alloy of antimony and lead of known antimony content. Such a solution, kept in a blue stoppered bottle, was re-standardised at the end of a month, and found to be practically unaltered. The following results show the effect of various impurities upon the accuracy of the method, the assay in each case being made in a similar manner:—

Antimony. Grm.	Added impurity. Per cent.	Bromate required. Cc.	Antimony, theoretical. Per cent.	Antimony, estimated. Per cent.
0·2	Nil	32·75	100·00	100·00
0·2	25 Fe	32·75	80·00	80·00
0·2	50 Fe	33·70	66·66	68·60
0·2	10 As	32·80	90·91	91·09
0·2	10 Sn	32·75	90·91	90·91
0·2	10 (As, Fe, Sn)	32·80	76·92	77·08
0·2	2·5 Cu	32·75	97·56	97·56
0·2	5·0 Cu	32·75	95·23	95·23
0·2	25 Cu	33·75	80·00	82·48

It is not common to have 10 per cent of any of the above impurities in a sample of hard lead. Small quantities do not affect the result to any appreciable extent. With 25 per cent of iron present it is difficult to tell the end reaction.

Hard Lead.—The sample, cast into a small ingot, is sawn obliquely through the middle with a fine saw, and the sawings sifted through a 30-mesh sieve. Weigh out 0·3 grm. of the sifted portion, place in a 16 oz. beaker, cover, and add 20 cc. strong hydrochloric acid, and boil gently for a few minutes; then while hot add a few cc. of a saturated solution of bromine in hydrochloric acid, and shake occasionally until the alloy is dissolved. The method is now exactly the same as that described in the standardisation of the bromate solution. Should a little chloride of lead crystallise out during the titration the result is not affected, but the liquid should not be allowed to cool too much. If the sample is boiled with hydrochloric acid alone, before adding the bromine, a saving of time is effected, and the results obtained are the same. The time taken for the assay is twenty-five minutes.

Sulphide ores, in which the antimony is completely soluble in hydrochloric acid and bromine, are treated as follows:—

Direct Method.—A small portion of the sample is crushed to pass completely through a 60-mesh sieve, and afterwards thoroughly mixed. 0·3 grm. is weighed into a 16 oz. beaker, and treated as described for alloys.

Oxide and Sulphide Ores, Soluble or Insoluble in Acids (Fusion Method).—0·3 grm. of the finely divided sample, intimately mixed with three or four times its weight of a mixture of equal parts of sodium carbonate and sulphur, is heated in a porcelain crucible, with lid, at a gentle heat for about fifteen minutes. The crucible and contents are allowed to cool, and the fused product is extracted with boiling water, and the solution filtered at the pump. The filter-paper, which contains the insoluble sulphides of copper, iron, &c., and possibly a little antimony, is transferred to a small beaker, and treated with a little hot hydrochloric acid. Now add caustic soda until nearly neutral, then sodium sulphide in excess, boil, and filter. The small quantity of antimony is now in solution and is added to the main bulk. (In the case of ores containing little impurities other than silica, the antimony is rendered completely soluble by the first fusion, and the above operation is unnecessary).

The antimony is precipitated as sulphide by the addition of hydrochloric acid, and the liquid warmed until the antimony sulphide settles. It is then filtered through a Gooch crucible, the bottom of which is covered with a layer of asbestos fibre. The sulphide is quickly filtered off, washed, and is then, together with the asbestos, transferred to a 16 oz. beaker, with the aid of a glass rod and a fine jet of strong hydrochloric acid. The volume of acid is made up to 25 cc., and boiled until the sulphuretted hydrogen is driven off. It is now cooled a little, a few drops of liquid bromine added, and boiled gently until the sulphur liquefies. Rinse the sides and cover of the beaker with a little cold water, filter through a small filter-paper, wash with a little hydrochloric acid, and, finally, with hot water. The filtrate is then boiled to remove excess of bromine, cooled, sodium sulphite added, and the antimony estimated as above. (Time taken for assay is one and a-half hours). The following examples show some results obtained:—

		Antimony. Per cent.
A. Sample of antimony oxide	Direct ..	82·34
	Fusion ..	82·24
B. Mixture of oxide and sulphide	Direct ..	55·73 (*a*)
	Fusion ..	56·73
	Gravimetric	56·80
C. Mixture of oxide and sulphide	Direct ..	60·89
	Fusion ..	60·83
	Gravimetric	60·92
D. Mixture of oxide and sulphide	Direct ..	61·53
	Fusion ..	61·58

(*a*) 1·0 per cent insoluble in acid.

Small quantities of antimony in slags, &c., can be estimated by first separating the antimony as sulphide, and treating as described above.

THE THERMO-CHEMISTRY OF NITROGEN.

By J. C. THOMLINSON, B.Sc. (A.Sc., Durham Coll. of Science).

FROM the large mass of thermo-chemical data available we have already shown conclusive reasoning for the existence of thermo-chemical equivalents for certain of the elements.

We are now considering nitrogen as regards its thermal relations in the compounds in which it occurs, but, in the first place, recur to the compounds hydrogen peroxide, H_2O_2, and ozone, O_3, which have the heats of formation given below:—

$$H_2 + O_2 = H_2O_2 + 45{\cdot}300 \text{ cals.} \quad . \quad . \quad . \quad \text{I.}$$
$$3O_2 = 2O_3 - 68{\cdot}000 \text{ cals.} \quad . \quad . \quad . \quad \text{II.}$$

The value H = 7·470 cals. for the heat of combination of hydrogen has already been found in a large number of cases to give, in the compounds in which it occurs, calculated heats of formation for these compounds agreeing with those found experimentally, and applying this value to Equation I., we obtain for oxygen in hydrogen peroxide a heat of combination O = 15·180 cals., the value already found for divalent oxygen being 52·545 cals.

In the three best known oxides of nitrogen, which we here represent with their heats of formation,—

$$N_2O \ldots \ldots \ldots \ldots = -17{\cdot}470 \text{ cals.}$$
$$NO \ldots \ldots \ldots \ldots = -21{\cdot}575 \text{ ,,}$$
$$NO_2 \ldots \ldots \ldots \ldots = -\ 2{\cdot}005 \text{ ,,}$$

it is evident since these all have a negative value that oxygen has probably in these compounds a very different thermal value from that found for divalent oxygen, and we are led by analogy to suppose that oxygen is other than divalent in hydrogen peroxide and ozone. Suppose, for example, that oxygen is quadrivalent in hydrogen peroxide, we should represent it structurally—

$$H_2 + O_2 = \begin{matrix} H-O \\ \| \\ H-O \end{matrix} + 45{\cdot}300 \text{ cals.}$$

from which it follows that quadrivalent oxygen has the value $O\equiv = 15{\cdot}180$ cals. already found, the difference between di- and quadrivalent oxygen amounting to 52·545 − 15·180 = 37·365. Hence, the addition of another bond to quadrivalent oxygen might be supposed to cause a further reduction of half this difference, or 18·683 cals., and pentavalent oxygen if such existed would have a value $O\equiv = 15{\cdot}180 - 18{\cdot}683$ cals. $= -3{\cdot}503$ cals.

In the molecule of oxygen, O_2, there is little reason for choosing between a di- or pentavalent character from a purely chemical point of view, and we might represent it O=O or $O\equiv O$, whence, reasoning from the latter of these formulæ, the thermal behaviour of ozone in changing to oxygen at once becomes clear. For if we represent oxygen as quadrivalent in ozone and pentavalent in the oxygen molecule, this reaction would be represented—

$$2O\begin{matrix} O \\ \| \\ O \end{matrix} = 3O=O + 68{\cdot}000 \text{ cals.}$$

in which six quadrivalent oxygen atoms become pentavalent, changing from a thermal value +15·180 cals. to −3·503 cals.; that is to say, by calculation a heat evolution equal to 11·677 × 6 = 70·062 cals. should take place, that found by experiment being 68·000 cals., the two figures showing a close agreement.

The application of this preliminary consideration of the thermal value and valency of oxygen will become clear when we deal with the oxides of nitrogen, but in this connection we will first take up the case of the cyanogen compounds and ammonia.

Hydrocyanic acid is formed with an absorption of heat, H + C + N = −27·480 cals., whilst for hydrogen and carbon we have already found thermo-chemical equivalents, H = 7·470 cals. and C≡ = −8·130 cals., from which it follows that in this compound the atom of nitrogen represents in the thermal equation a heat absorption, N = −26·820 cals., which value applied to the compound cyanogen, C_2N_2, gives a calculated heat of formation, −16·260 cals. − 53·640 cals. = −69·900 cals.; that found by experiment being −65·700 cals.

Here, again, we have an agreement between theory and experiment, and will now turn to ammonia, NH_3, which is formed with an evolution of heat, $N + H_3 = NH_3 + 11{\cdot}890$ cals., from which the thermal value of the nitrogen atom is found to be $-(3 \times 7{\cdot}470 - 11{\cdot}890) = -10{\cdot}520$ cals.

These values for nitrogen in hydrocyanic acid and ammonia, together with the knowledge that cyanogen forms well characterised normal and iso-compounds, in the latter of which it must be regarded as pentavalent, would justify us in believing nitrogen to be pentavalent in the comparatively unstable compounds hydrocyanic acid and cyanogen, and trivalent in ammonia.

Thus, N≡ = −26·820 cals. and N≣ = −10·520 cals., and we will find that these values are fully borne out when applied to the oxides of nitrogen, the formulæ of which have already been given.

If in nitrous oxide, N_2O, oxygen be represented as pentavalent, but with the difference that in the structural formula shown below, in which nitrogen is trivalent, there is one oxygen bond of valency which forms a central union in the molecule, without affecting the trivalency of nitrogen, and which bond is equivalent to a heat evolution, +3·503 cals., instead of the absorption, −3·503 cals., for pentavalent oxygen referred to as possible when considering ozone, then such a bond would account for the comparative stability of nitrous oxide, and the heat of formation of this compound would be 2 × −10·520 + 3·503 = −17·537 cals., the experimental value for the heat of formation of nitrous oxide being = −17·470 cals.

$$\begin{matrix} N- \\ \| \\ N\equiv \end{matrix} O = -17{\cdot}470 \text{ cals.}$$

This assumption of a central bond of union is not only justified by the stability of nitrous oxide, but the positive value given to it would merely represent the amount of heat given out by a pentavalent atom in a molecule of oxygen if the thermal relations supposed above in connection with ozone were correct on the rupture of this molecule.

Similarly, in nitric oxide in which we regard nitrogen and oxygen as pentavalent with the formula N≣O, and where, again, we represent a similar central bond of union by a thickened line in the formula, we should expect a heat of formation, −26·820 + 3·503 = −23·317 cals., the value found by experiment being −21·575 cals.

Nitrogen dioxide may be represented by the structural formula—

$$N\begin{matrix} O \\ \| \\ \equiv O \end{matrix} = -\ 2{\cdot}005 \text{ cals.;}$$

in which nitrogen is trivalent, and oxygen pentavalent, the two atoms of oxygen in this case contributing to form the central bond of union, and hence giving a heat of formation of this compound, −10·520 + 2 × 3·503 cals. = −3·514 cals., the experimental value being −2·005 cals.

In viewing these three oxides of nitrogen we feel justified from the agreement of theory and experiment in giving them the structural formulæ here represented, especially when we consider the order of their stability, nitrous oxide being most stable, nitric oxide least so, and nitrogen dioxide intermediate between the two, and also the fact that nitrogen dioxide is formed by the mere contact of nitric oxide with atmospheric oxygen, the formation of the dioxide taking place under just such conditions as here represented.

Further, in giving a numerical value to the part played by oxygen in forming a central bond in these compounds we do not pretend to anything more than approximation.

We conclude by giving a comparative statement of the results obtained by theory as shown against those actually found experimentally.

	Experimental value.	Theoretical value.
$2O_3 = 3O_2$ ..	+68·000 cals.	70·062 cals.
$C_2 + N_2 = C_2N_2$ ..	−65·700 ,,	−69·900 ,,
$N_2 + O = N_2O$ ..	−17·470 ,,	−17·537 ,,
$N + O = NO$ ..	−21·575 ,,	−23·317 ,,
$N + O_2 = NO_2$ ..	−2·005 ,,	−3·514 ,,

CALCIUM AS AN ABSORBENT OF GASES FOR THE PRODUCTION OF HIGH VACUA AND SPECTROSCOPIC RESEARCH.*

By FREDERICK SODDY, M.A., Lecturer in Physical Chemistry in the University of Glasgow.

(Concluded from p. 45).

Appendix.—*Results of Gauging High Vacua by the Evaporation Test.*

By Arthur John Berry.

In this note the results of some experiments, on the rate of evaporation of liquid air contained in a Dewar vessel exhausted in different ways, are described with the view to showing that this test may be used as a means of gauging the degree of vacuum produced by different processes. Owing to various causes the research has not been carried as far as it was intended, but one set of measurements, complete in themselves, have been obtained which bear out in a clear manner one of the points discussed by Mr. Soddy in the paper preceding. Starting with a vessel filled with air at atmospheric pressure, there is no difficulty, by using the method of Sir James Dewar to produce a vacuum therein, in obtaining a vacuum apparently perfect, so far as the electric discharge test can indicate, provided that a sufficiency of charcoal is employed. It was of interest to compare the rate of evaporation of liquid air in a Dewar vessel exhausted in this manner, with the rate in the same vessel exhausted also by Dewar's method, but in which the air had been first removed by an auxiliary pump. Although the electrical test reveals no difference in the degree of vacuum obtained in the two methods, it is to be expected that the thermal test will show a far higher vacuum by the second method than by the first, owing to the residuum of non-conducting inert gases left by the first method (compare Lord Blythswood and H. S. Allen, *Phil. Mag.*, October, 1905, p. 497). This expectation has been fully borne out by the experiments.

The vessel employed was of about 1 litre capacity, globular in form, and silvered on the two inner walls. During the exhaustions it was placed in an inverted position in an air oven, and the temperature maintained at 350 C. A vacuum-tube served to indicate the progress of the exhaustion. At the completion of each exhaustion it was filled with liquid air, and kept in an ice chest to keep the external temperature constant. The vessel was weighed at regular intervals to determine the rate of evaporation of the air. Three different methods of exhaustion, designated throughout I., II., III., were employed.

I. In the first the exhaustion was performed by the mercury pump. A Töpler pump of ordinary pattern, worked by hand, was used, and pumping was continued from four to five hours while the vessel was heated in the air oven. The pump had a capacity of about 350 cc., and was provided with a phosphorus pentoxide tube and tap. The results of two similar experiments agreed well among themselves, and in the table the second of the two, which was slightly the better, is alone included.

II. In the second method the apparatus was exhausted from atmospheric pressure by cooled charcoal. As in the experiments of Lord Blythswood and Mr. H. S. Allen (*loc. cit.*) two separate charcoal bulbs were employed, the one with 97 grms. and the other with 70 grms. of charcoal freshly prepared from cocoanut shells. The first bulb alone reduced the pressure from atmospheric to the fluorescent stage in thirty minutes, and was then cut out and the second bulb brought into action. The absorption was continued one and a half hours further, and the vessel sealed off. No discharge could be sent through the vacuum-tube at this stage.

III. The same vessel was exhausted by a duplex Fleuss pump of large size, mechanically driven, and during the action of the pump the charcoal was well heated. In this way carbon dioxide is expelled from the charcoal, and the last traces of air are swept out. It was found in a separate experiment that little or no difference was produced in the result by the displacement of the last of the air by oxygen during pumping. In this method only one charcoal bulb was used, which was connected direct by a glass tube without taps to the vessel being exhausted. The connection with the pump was sealed after the removal of the air was judged complete, and the absorption by charcoal continued for two and a half hours.

The following table shows the results of the three methods. Weighings were taken at intervals of either six or twelve hours. The first column shows the time in hours from the first weighing, and the total weight of liquid air initially present in the three experiments is indicated in the first line. The succeeding lines indicate the amount that has evaporated in the six or twelve-hour interval from the previous weighing:—

Hours.	I. (*a*)	II.	III.
0	972 grms.	954 grms.	979 grms.
12	2×54·5	2×63	2×40·5
18	54	62	40
24	54	60	39
36	2×54·5	2×60	2×39
42	54	59	39
48	55	58	37
60	2×56	2×57·5	2×37
66	56	57	37
72	57	56	37
84	2×58·5	2×56	2×37
90	58	55	38
96	59	56	36
	(78 remaining)	(18 remaining)	
108	—	—	2×37
114	—	—	38
120	—	—	36
132	—	—	2×36
138	—	—	36
144	—	—	37
			(78 remaining)

(*a*) The slight increase in the rate of evaporation during this experiment is due to a shortage in the supply of ice in the ice-chest. In the other two experiments the chest was kept well filled.

It will be seen at a glance that whereas the vacuum resulting in the second method, by cooled charcoal, but starting from atmospheric pressure, is inferior to that produced by a simple mercury pump, that obtained in the third method, by charcoal after removal of the air, is by far the best of the three. After six days 78 grms. of liquid air out of the original kilogramme remain in the vessel.

In conclusion, I desire to take this opportunity of expressing my indebtedness to Mr. Soddy, at whose suggestion the research was undertaken, for placing the apparatus required at my disposal and for many valuable suggestions.

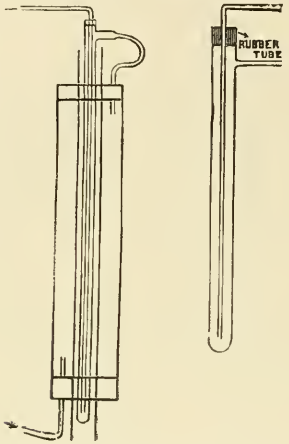
* Read before the Royal Society, November 15th, 1906

IMPROVED LIEBIG'S CONDENSER.

By HENRY R. ELLIS, B.Sc., F.C.S.

THE following is a description of a very simple device for improving the efficiency of a Liebig's condenser when used as a reflux with volatile liquids:—

By inserting in the middle tube of the condenser a tube, as shown in the figure, and passing the water from the



outer tube of the condenser through this, the cooling surface is much increased.

BORIC ACID: ITS DETECTION AND DETERMINATION IN LARGE OR SMALL AMOUNTS.*

By WILSON H. LOW.

MANY good articles have been published on the detection and determination of boric acid, but they are rather fragmentary in character, and while helping in one direction, have left much to be desired in another. Most processes are tedious of execution, and do not give evidence that all the boric acid will be obtained.

I have discovered two points in regard to the detection and determination of boric acid which I believe are new.

One of these is that in the qualitative test it is not necessary to dry the turmeric paper at the temperature of the water-bath, but that the test carried on at the ordinary temperature in the air or vacuum desiccator, or even at 40° to 50° in a desiccator, is exceedingly delicate, and allows the detection of boric acid in the presence of large amounts of other salts, and in the presence of such interfering agents as nitrates and phosphates, when it would be entirely overlooked by the ordinary methods.

I do not know the limit of the qualitative test, but such small quantities of boric acid as 0·000001 grm. in 1 cc. or 0·0000001 grm. in 0·10 cc. are easily recognised, and these same quantities would undoubtedly be recognised by the evaporation of larger quantities of the solvent.

The other point applies to the quantitative determination. It is very difficult to distil off all the boric acid from an aqueous solution, by passing the vapour of methyl alcohol through it. As long as any quantity of water remains it will retain boric acid, but it has been found that, by adding some substance to unite with the water, it is possible to distil off the total boric acid easily and with no tedious evaporation to dryness, with the attendant bumping and danger of breakage. Such a substance is the dry, granulated, chemically pure calcium chloride.

The methods described below have been in use about three years, and a great many experiments have been made to test the various points brought out. Further experiments will bring out other points of value, but the methods are in good shape, and if followed as directed, will give the desired result. The methods will first be given as they are expected to be carried out, and further on will be given the experiments, or some of them, on which the processes stand. The action of indicators in the presence of boric acid and in the presence of methyl alcohol will also be given.

Wherever methyl alcohol is mentioned, the laboratory refined Columbian or Colonial spirits of commerce is meant. In the refined state, as it is purchased, it contains boric acid, and this has to be removed, and the alcohol tested to make sure it is entirely free from it.

Qualitative Test.

The test is given as applied to meat products, but obviously it may be applied to anything where the boric acid can be obtained in a soluble form. Ten grms. of the hashed meat are placed in a metal dish (the cover of a three-pound lard pail is as good as anything, if well cleaned), and moistened with 5 cc. of a N/2 solution of sodium carbonate or its equivalent. Place on the steam-bath or in an oven till about dry. Drying may be done nicely on a small electric stove. Ignite the dry mass, over a burner that heats the whole bottom of the dish evenly. Do not use a high heat. Thoroughly carbonise the ash, but do not bother to burn off much of it. Burning off is dangerous, as boron compounds may be volatilised when ignited in the presence of carbon. Direct experiments have shown this. The carbonised ash is placed in a mortar (a glass mortar is best), and ground up somewhat, and then about 10 cc. of water containing 1 cc. of strong hydrochloric acid added, and triturated with it. Filter off through a small filter (a small Witt's plate is best, as it retains very little liquid) into a flat platinum or glass dish. A Petri dish 7—10 cm. in diameter is good.

About 1 cc. or less of the solution is taken and placed in a watch-glass, and evaporated on the steam-bath with a piece of turmeric paper. If boric acid is present in the food product as a preservative, and there are no interfering agents, such as nitre, present, then a test for boric acid will be obtained here. This does not mean that if a test is obtained here the food product necessarily contained boric acid added for preserving purposes, but merely that the test is delicate enough to detect any possible amount of boric acid that would be added intentionally. The main lot of solution is placed in a shallow dish with a piece of turmeric paper, and then placed in a desiccator till *perfectly* dry. A vacuum drying oven is best, as the drying is rapid. I use a vacuum drying oven, and can control the heat, using generally 40° to 50°, and about 700 mm. vacuum. The smallest traces of boric acid will show up in this test. It is more delicate, if anything, if the drying is done in an ordinary desiccator, but the time of drying is very long. Tests that fail utterly on the steam-bath will show up strongly under these conditions. Nothing which I have tried, such as nitre, salt, sulphates, or even phosphoric acid, has interfered with the test. Nitre will destroy the test carried on on the steam-bath, and many other salts will seriously interfere. Make sure the turmeric paper is perfectly dry, for incrusting salts often give the appearance of dryness while the underlying paper is still moist. Food products should not be con-

* From the *Journal of the American Chemical Society*, xxviii., No. 7.

demned because a strong test is obtained by operating in this manner. Added boric acid is easily detected by moistening the turmeric paper with the solution and drying on the steam-bath. If nitre is present, it can be gotten rid of (for the steam-bath test) by igniting with sufficient organic matter, or, better, by distilling off the boric acid with methyl alcohol, and testing the distillate. In testing qualitatively, the best result seems to be given with a solution containing at least one-tenth its volume of free strong hydrochloric acid, if the test is made on the steam-bath. For the test at ordinary temperature or at 40° to 50°, a slight excess of acid is all that is needed, though greater excess does no harm. For the delicate test I should advise against the use of the trade mark glasses, as they are borosilicates, and I have some indications that they will give up boric acid.

In the following tests the final volume before evaporation was 2 cc. unless otherwise stated. The turmeric paper was about 50×9 mm., and the ordinary paper supplied by chemical dealers. A steam-bath was used with the first twenty tests.

The last test repeated on the steam-bath will bleach the paper owing to the formation of chlorine compounds.

Many other tests have been tried, and nothing found to interfere with the test made by drying in the vacuum desiccator or oven.

There appears to be no loss of boric acid in concentrating a large volume of solution in the vacuum, and the test is just as strong as where only 1 cc. is used. 0·00001 grm. of boric acid is equivalent to 0·0001 per cent when 10 grms. of material are operated on, and this qusntity is infinitesimal for a preservative. As far as that is concerned, the simplest kind of a test, carried out in the roughest manner, is amply delicate to detect any boric acid added for preserving purposes. The exception to be noted is where there is a nitrate present.

Quantitative Test.

Reagents.—Methyl alcohol free from boric acid; methyl-orange indicator; *p*-nitrophenol indicator; phenolphthalein indicator; hydrochloric acid free from boric acid; calcium chloride, granulated, chemically pure; standard solution of sodium hydroxide, as free as possible free from carbonate; standard solution of sulphuric acid, as free as possible from carbonate; whether these solutions are normal or of other strength depends on what quantity of boric acid is being dealt with. Both normal and tenth-normal are useful.

Standard Solutions.—The standard solutions of acid and alkali are made up in the Laboratory of the Cudahy Packing Company from distilled water which has been distilled from a block-tin (solid) still and condenser, and subsequently boiled hard for about twenty minutes in another block-tin vessel furnished with a connection to a large soda-lime column. After boiling, the vessel is furnished with a tin condensing pipe inside to cool the water rapidly. All air entering the vessel has to come through the soda-lime column, and the water keeps free from carbonic acid. While 100 cc. of the ordinary distilled water will take about 15 drops of N/10 sodium hydroxide solution to give a *permanent* coloration with phenolphthalein, the boiled water allows the permanent coloration to show up strongly with one drop, and this is almost sufficient for a litre of the boiled water. Incidentally, I will remark that sodium thiosulphate solutions made up with this water will keep their correct strength almost indefinitely, and deposit no sulphur.

Preparation of the Methyl Alcohol.—"Columbian" or "Colonial Spirits" are introduced into a still of some kind, and made *strongly* alkaline with some very concentrated caustic soda or potash. If a glass vessel is used, it must be furnished with a capillary boiling tube, and the size of this tube adapted to the size of the flask, &c. (see Heyward Scudder, *Journ. Am. Chem. Soc.*, xxv., 163).

Test.	Final volume of solution. Cc.	Boric acid present. Grms.	Excess of strong HCl. Drops.	Other things present.	Indications.
1.	2·00	0·0000000	2	Nothing	None
2.	2·00	0·0000010	2	Nothing	Merest trace
3.	2·00	0·0000100	2	Nothing	Strong test
4.	2·00	0·0000050	2	Nothing	Strong test
5.	2·00	0·000025	2	Nothing	Slight test
6.	2·00	None added	2	1 cc. N/1 NaOH	None
7.	2·00	0·0000025	2	1 cc. N/1 NaOH	None
8.	2·00	0·0000050	4	1 cc. N/1 NaOH	Slight trace
9.	2·00	0·0000100	4	1 cc. N/1 NaOH	Mere trace
The above tests show the sensitiveness without interfering substances present, and also how sodium chloride interferes when present.					
10.	2·00	0·0000050	2	5 cc. $Ba(OH)_2$	No test
11.	2·00	0·0000100	4	1 cc. N/1 NaOH	Mere trace
12.	2·00	0·0000100	2	Salt from 1 cc. N/1 NaOH	Mere trace
13.	2·00	0·0000150	2	Nothing	Good test
14.	2·00	None added	2	Salt from 1 cc. N/1 NaOH	Trace
15.	2·00	0·0000100	10	Salt from 1 cc. N/1 NaOH	Slight trace
16.	2·00	0·0000200	2	Salt from 1 cc. N/1 NaOH	Slight trace
17.	2·00	0·0000200	10	Salt from 1 cc. N/1 NaOH	Slight test
18.	2·00	0·0000250	2	Salt from 1 cc. N/1 NaOH	Slight test
19.	2·00	0·0000300	2	Salt from 1 cc. N/1 NaOH	Plain test
20.	2·00	0·0000100	2	15 grms. of sand + 2 cc. of curcuma solution	Faint test
The following tests were made at the ordinary temperature or not to exceed 40° C. Either a vacuum drier or an ordinary desiccator was used. V = vacuum drier and D = desiccator.					
21. V	2·00	0·0000100	2	Salt from 1 cc. N/1 NaOH	Strong test
22. V	2·00	0·0000010	2	Salt from 1 cc. N/1 NaOH	Plain test
23. D	1·00	0·0000010	1	Nothing	Strong test
24. D	0·10	0·0000001	½	Nothing	Plain test
25. V	10·00	0·0000100	1	1 cc. saturated solution Na_2CO_3 ..	Strong test
26. V	10·00	0·0000100	1	1 drop of syrupy phosphoric acid ..	Strong test
27. V	10·00	0·0000100	1	1 cc. potassium nitrate solution ..	Strong test

Distil off the alcohol carefully, and run a blank through the apparatus (putting alkali in the boiling flask), and see if there is any titratable amount of boric acid given off. If not, the alcohol is all right. Where the alcohol is to be used to collect the boric acid for a subsequent qualitative test, it must be purified till 100 cc. of distillate give no test for boric acid qualitatively.

Effect of Methyl Alcohol on p-*Nitrophenol and on Phenolphthalein.*—The alcohol recently distilled from an excess of alkali is meant in all cases. 100 cc. of the alcohol were taken, and one drop of the nitrophenol indicator added. The colour was yellow. N/10 sulphuric acid was run in till the solution was colourless. 0·90 cc. was used. One drop of N/1 sodium hydroxide brought back the yellow very strong. Experiment repeated except N/1 sulphuric acid was used. Result the same, two drops = 0·10 cc. being used. This relationship between one drop of nitrophenol and methyl alcohol holds roughly for various dilutions, and a delicate method of testing for acidity in methyl alcohol might be arranged from this fact. In our case all we wanted was to make sure that we could titrate the mineral acid in the methyl alcohol distillate fairly close, and this is demonstrated.

Phenolphthalein is of little use in titrating acidity in methyl alcohol. Great dilution is necessary before the indications are good. But after the alcohol is made neutral or slightly alkaline (after previously being acid) to nitrophenol, then phenolphthalein may be depended on to indicate pretty closely the end-point for a boric acid titration.

Indicators.—Phenolphthalein is made up by dissolving 5 grms. in 500 cc. of ethyl alcohol, and making up to 1 litre. Use about 1 cc. in tests.

p-*Nitrophenol.*—This indicator was ordered as nitroso-phenol, and came marked as nitrosophenol, but as it fails to give Liebermann's reaction for nitroso compounds, and has a melting-point of about 113° it must be simply *p*-nitrophenol and not the nitroso-compound.

Make up by dissolving 1 grm. in 75 cc. of neutral ethyl alcohol, and add 25 cc. of water. Use 1 drop to 100 cc. of the solution to be titrated. As this indicator is, perhaps, not well known I will give its properties as I have found them. My attention was first called to this indicator by an article by L. Spiegel in the *Journ. Chem. Soc. Ind.* (1900, xix., 1049). He recommends it to replace methyl-orange. I can corroborate his statement, and also those he makes in the same journal (xxiii., 682), where he takes issue with Lunge on its being able to replace methyl-orange for many titrations. This indicator is about as sensitive as phenol phthalein. Colourless with mineral acids and intensely yellow with caustic or carbonated alkalis. With bicarbonates the yellow shade is much weaker, but still bicarbonates can be titrated, if care is used. In boric acid titrations, avoid carbonates as much as possible. If 100 cc. of water is made just alkaline to nitrophenol, on adding glycerol the solution becomes colourless when boric acid is present, though boric acid gives no indication in aqueous solution, unless it is a strong solution, in which case even methyl-orange will react acid. No distinct end-point can be obtained with nitrophenol in the presence of glycerol and boric acid. As the boric acid comes nearer to $NaBO_2$ the colour of the solution becomes more intensely yellow, and this acts as a guide to the phenolphthalein end-point.

Methyl-orange.—One grm. dissolved to 1 litre in water. It may be used in place of nitrophenol in aqueous solution, but not in methyl alcohol. It has the advantage over nitrophenol of being less sensitive to carbonic acid (though it is by no means entirely indifferent to this acid), and also less sensitive to boric acid in a strong aqueous solution. Its disadvantages are that it is not nearly as sensitive as nitrophenol, and the end-reactions run through several shades of colour, and it cannot be used in methyl alcohol with any accuracy. I seldom use it for boric acid titrations.

We have found that methyl-orange and nitrophenol give he same end-points in titrating sodium hydroxide or ammonia. Remember always that the colour is much weaker in the presence of bicarbonates.

In the absence of interfering agents and complete absence of carbonic acid, phenolphthalein, methyl-orange, and nitrophenol in aqueous solution will give identical end-points.

(To be continued).

ON THE ELEMENTARY NATURE AND ATOMIC WEIGHT OF TELLURIUM.*

By JAMES F. NORRIS.

Some years ago Norris, Fay, and Edgerly undertook a study of the elementary nature of tellurium in order to discover, if possible, the cause of the anomalous relation of the element to the periodic law (*Am. Chem. Journ.*, xxiii., 105). Up to the time of the publication of the work reported by them, no systematic study of this problem had been described. A number of investigators had determined the atomic weight of tellurium, after what appeared to be a careful purification of the compounds to be analysed. The methods of purification used, however, were not of such a nature as to be relied upon to free the compounds investigated from undiscovered elements. With this fact in mind an investigation was undertaken. Since the work was started great activity has been shown in this field, and a number of papers have appeared on the atomic weight of tellurium. The most noteworthy is that of Köthner, to which the reader is referred for a full historical account of the subject (*Ann.*, cccxix., 1).

The work about to be described was inspired by a statement in the Faraday memorial lecture delivered by Mendeléeff in 1889. In discussing the periodic law Mendeléeff recounts the great service which the law has rendered in bringing about the correction of a number of atomic weights. In seeking to explain the high value of the atomic weight of tellurium, he expresses the opinion that the so-called element consists of two elements: one, true tellurium with an atomic weight of approximately 125, and the other, an element with a higher atomic weight, which would find a place in the periodic classification in the vacant space under tellurium. To this undiscovered element Mendeléeff gives the name dvitellurium. He sketches the chemical and physical properties of such an element, as he had already done so successfully in other cases.

It was to test this hypothesis that the work which has been published and that described below were undertaken. In order to make the study of the problem complete it seemed necessary to endeavour to discover, first, whether an undiscovered element, which did not belong to the sulphur group, was present in tellurium, and, second, whether the hypothesis of Mendeléeff could be given any experimental basis.

In seeking a solution of the first problem, a sample of tellurium, which had been freed from all known elements, was converted into a compound of the formula $Na_2S_4TeO_6$. This substance is a derivative of sodium pentathionate in which one sulphur atom has been replaced by one of tellurium. From this compound the tellurium was recovered by means of a reaction which is characteristic of pentathionates. Determinations of the atomic weight of the tellurium, which had been purified in this way, gave as a mean from several experiments the value 127·46. (For the atomic weights used in the calculation see *prox.*; if no vacuum correction is made and 14·04 is taken as the atomic weight of nitrogen this value becomes 127·62). This number was identical with that obtained with a sample of the element which had not been subjected to this particular method of treatment. As it is improbable that an element not in the sulphur group would show the

* From the *Journal of the American Chemical Society*, xxviii., No. 12.

power to replace, in part, sulphur in such a characteristic compound as sodium pentathionate, the conclusion can be drawn that tellurium contains no element which does not show the characteristic reactions of the sulphur group.

In order to test experimentally the hypothesis of Mendeléeff, carefully purified compounds of tellurium were subjected to fractionation. In the paper already published an account is given of the study of the products resulting from a fractional crystallisation of the double bromide of tellurium and potassium. Atomic weight determinations of the element obtained from these products agreed with one another within the limits of accuracy of the method used. Notwithstanding this result the work was continued, as it was thought that the breaking down of the salt by crystallisation might not have been effected on account of the fact that its constituents were isomorphous with each other. The method described below, which was finally selected to test the question, involved the study of the products resulting from the fractional distillation of tellurium dioxide.

Other investigators have used compounds which have been distilled. Brauner used sublimed tellurium tetrabromide in one of his atomic weight determinations. As the difference between the boiling-points of the bromides of selenium and tellurium is not great, it is evident that a long-continued process of fractionation would be necessary to free tellurium bromide from the analogous compound of dvitellurium. Since this work was started Köthner has determined the atomic weight of distilled tellurium. The difference between the boiling-points of selenium and tellurium is such that it would be reasonable to expect that another element in the same family with a higher atomic weight would have a boiling-point not far from that of tellurium. It appeared from the above-mentioned facts that it was worth while to re-study the problem if a better method could be found. The properties of the oxides of sulphur, selenium, and tellurium are such, that it seemed that a study of tellurium dioxide would give results which would furnish a definite answer to the question as to the elementary nature of tellurium. Sulphur dioxide boils at −8°, selenium dioxide is volatile at 200—250°, and tellurium dioxide is converted into vapour slowly at a bright red heat. In the light of these facts it is highly probable that the oxide of another element in the same family, with a higher atomic weight, would be very much less volatile than is tellurium dioxide, if volatile at all at the temperature of the Bunsen flame.

The oxide investigated was prepared from a sample of nitrate which had been carefully purified. The source of the material and the methods of preparation and purification used are described in detail in the paper cited above. In the distillation of the oxide the process was stopped after about three-quarters of the product had been volatilised. The part which had distilled was re-distilled until, as before, three-quarters of it was collected. This process of fractionation was repeated five times. The oxide was distilled from platinum at the highest temperature obtainable with a Bunsen burner; under these conditions the oxide was collected at the rate of about 0·15 grm. per hour.

The atomic weights were determined of the tellurium in the first residue, which should have contained the less volatile oxide, and of the tellurium in the oxide which had been sublimed five times. As a standard for comparison the atomic weight of the tellurium in a sample of oxide which had not been sublimed was determined. The method of determining the atomic weight which was used was that first described in the paper by Norris, Fay, and Edgerly, already cited, namely, the conversion of the nitrate into the oxide. This method has recently been used with success by Köthner.

The results were as follows:—The average atomic weight obtained in the case of the tellurium from the undistilled oxide was 127·50. The average of three determinations of the value, when the oxide which had been distilled five times was used, was also 127·50. The original residue from the first fractionation gave the atomic weight 127·46. It is evident from these results that the fractional distillation effected no decomposition in the tellurium dioxide. The mean of all the values for the atomic weight agrees well with the most trustworthy determinations which have been published, when these are calculated on the same basis.

The results seem to the writer to furnish positive evidence in favour of the elementary nature of tellurium. With a difference of about 250° between the boiling-points of sulphur dioxide and selenium dioxide, and a difference of 500° to 600° between the same constants for selenium dioxide and tellurium dioxide, it is evident, from all analogies in the properties of compounds of members of the natural families in the periodic classification, that the oxide of an element, which should find its place in the formulation of the law in the vacant space under tellurium, should be very much less volatile than tellurium dioxide. Its separation by the process used should have been at least in part effected. Even if tellurium contains an element which does not belong to the sulphur family, the possibility of its oxide having the same volatility as that of tellurium dioxide is very remote. As there was no evidence of even the slightest change in the properties of the compound, or in the atomic weight as a result of the tests applied, and as these tests seem to be reliable and well suited to answering the question, the conclusion can be drawn that the statement that tellurium is an element rests upon a firmer experimental basis than heretofore.

Experimental.

The source and preliminary purification of the material used in this investigation are described at length in the paper already cited. A sample of the basic nitrate of tellurium, which had been re-crystallised three times from nitric acid, was made use of in the work. From this the oxide was prepared by heating at increasing temperatures until all nitric acid had been removed.

About 25 grms. of the oxide were fractionally distilled. The point at which tellurium dioxide volatilises is so high it could not be distilled in a tube in the usual way. After tests of a number of methods that selected was as follows:—The oxide was heated to bright redness in a platinum crucible, over which was placed a funnel with the stem bent at right angles. To this last was attached a glass tube provided with a cork and an exit tube, the open end of which was covered with filter-paper. A rapid stream of air was drawn through the tube and funnel. The tellurium dioxide which had been vaporised was swept through the funnel, and was collected as a fine powder, which settled in the tube and on the paper which covered the exit from the tube. When the crucible, which contained the oxide, was heated to bright redness, between 0·1 and 0·2 grm. of the oxide distilled in one hour.

The distillation was started with about 25 grms. of tellurium dioxide. This was heated until a residue of 7 grms. remained. The 18 grms. which had been vaporised were again distilled until there was a residue of about 3 grms. The twice distilled oxide was re-distilled until about 12·5 grms. had been collected. The process was repeated and 8 grms. were distilled off. In the fifth distillation the oxide which was collected weighed about 6 grms. The fractions of the oxide resulting from the distillation were converted into the basic nitrate, re-crystallised twice from nitric acid, and finally purified for analysis as described below.

(The author gladly acknowledges his indebtedness to Mr. C. F. Swan, of the Massachusetts Institute of Technology, who carried out the fractioning of the oxide, which was a tedious process, requiring a very long time for its completion).

In endeavouring to test the question whether tellurium contains an unknown element which does not belong to the sulphur group, another method of purification was made use of. Facts which were reported by Norris and Fay in their papers on the volumetric estimation of

selenium and tellurium suggested a convenient way of attacking this problem. It was shown that a reaction represented by the following equation takes place when selenium dioxide, sodium thiosulphate, and hydrochloric acid are brought together in aqueous solution :—

$$SeO_2 + 4Na_2S_2O_3 + 4HCl = Na_2S_4O_6 + Na_2S_4SeO_6 + 4NaCl.$$

The selenopentathionate is very unstable and cannot be obtained from solution. That the salt was present was shown by the fact that the solution exhibited all the reactions which are characteristic of pentathionates. Sodium pentathionate is stable in an acid solution, but is instantly decomposed when brought into contact with alkalis, being converted into sodium tetrathionate and free sulphur. The analogous selenium compound suffered decomposition in the same way, and was converted into the tetrathionate and selenium.

It was also shown that similar reactions take place when the product of the reaction between tellurium dioxide, sodium thiosulphate, and hydrochloric acid is treated with alkalis. A sample of pure tellurium dioxide was converted into the pentathionate derivative, which was then treated with sodium hydroxide. It seemed highly probable that the precipitated teliurium so obtained was free from any element which did not have the power to replace sulphur in a pentathionate. The precipitate was treated with hydrochloric acid to free it from any hydroxide that may have been thrown down by the alkali.

In order to carry out the reaction successfully the substances are brought together in the quantities required by the chemical equation, with the exception that more hydrochloric acid than is called for must be used in order to keep the tellurium dioxide in solution. The solution must be dilute and cold in order to prevent decomposition of the sodium thiosulphate by the excess of acid. Addition of a small quantity of alkali to the acid solution causes the precipitation of a part of the tellurium present. This precipitation continues until the solution is rendered alkaline. The tellurium obtained in the way outlined above was converted into the basic nitrate, which was crystallised twice and finally prepared for analysis.

In the final purification of the nitrate it was crystallised from dilute nitric acid (sp. gr. 1·25), which was prepared from purified materials. The water used for dilution was twice distilled, the last time from alkaline permanganate. The nitric acid used was a good sample of chemically pure acid, which was re-distilled slowly from a platinum still, provided with a platinum condenser and receiver. The diluted acid was kept in bottles which had been repeatedly treated with warm nitric acid. The salt was crystallised in porcelain dishes which had been carefully cleaned with hot acid. Saturated solutions of the salt were evaporated at about 85° until reduced to about one-fourth their original bulk. The hot mother-liquor was immediately removed, and the crystals were washed with re-distilled concentrated nitric acid. The crystals were again dissolved in the purified acid, and re-crystallised.

It was found necessary, in order to obtain concordant results, to use, in determining the ratio between the weights of nitrate and oxide, only crystals which had been formed during the evaporation. In every case where the mixture of crystals and mother-liquor was allowed to stand over night before the crystals were removed, low values of the atomic weight, which varied with different samples, were obtained. It was evident that spontaneous evaporation caused the formation of crystals which contained mother-liquor.

The crystals which were removed from the hot solution were washed a number of times with re-distilled concentrated nitric acid, and were then ground to a very fine powder in an agate mortar, while still moist with acid. The finely ground nitrate was transferred by means of a platinum spatula to a well-cleaned porous tile, which immediately removed most of the acid clinging to the powder. The tile, with the nitrate which had been placed on it in a small pile, was placed in a desiccator which contained concentrated sulphuric acid and solid potassium hydroxide. The air was exhausted from the desiccator, which was left undisturbed for a day. The nitrate was then removed from the tile, care being taken to reject the portion which had come in contact with the tile. The product, which was at this stage in the form of a hard lump, was readily reduced to a find powder by breaking it with a few strokes of a spatula. The nitrate was next kept for at least three days in a vacuum over phosphorus pentoxide.

This method of removing the excess of acid liquid from the nitrate is an improvement over that used by Köthner in his work. Köthner was of the opinion that as the acid was removed by evaporation from the crystals, they were partially decomposed to the oxide with loss of acid. This may have been the case when the acid was removed at an elevated temperature as Köthner did it. In order to prevent this decomposition he washed the crystals with mixtures of nitric acid and alcohol, using successively a larger proportion of alcohol in the mixture until pure alcohol was used. This method is tedious, and great precautions are necessary. In the preliminary work a number of samples were prepared by Köthner's method. These gave the same results as samples prepared as described above.

In determining the ratio between the weights of the nitrate and oxide the usual precautions necessary for accurate results were taken. The weights were calibrated and a balance sensitive to 0·03 mgrm. was used. The weighings were made by substitution after the crucibles had stood in the balance case at least two hours. A crucible like those used to contain the nitrate was used as a tare.

The samples of nitrate were heated in platinum crucibles to constant weight at 140° in a current of air dried by passing over phosphorus pentoxide. The first heating of the salt, which brought it to constant weight, was continued for four hours. The samples were weighed before and after this heating at 140°. In no case was the loss in weight as a result of heating for four hours greater than 0·1 mgrm. The decomposition of the nitrate was brought about slowly in order to avoid the loss of tellurium dioxide by mechanical removal along with gases evolved. The crucibles were heated about six hours at 250°, six hours at 300°, three hours at 350°, three hours at 400—450°. The crucibles, resting on pieces of platinum-foil inside a large covered porcelain crucible, were next heated for four hours at the highest temperature procurable with a Bunsen burner. The oxide formed from the nitrate in this way was finally fused by the application of a free flame for a few seconds. A test showed that the oxide contained no nitric acid, and the glassy condition produced by the fusion precluded the possibility of any enclosed gases.

The results of the analyses follow :—

No.	Weight $2TeO_2.HNO_3$.	Weight TeO_2.	Atomic weight.
1.	2·28215	1·90578	127·47
2.	2·35429	1·96615	127·53
3.	1·86853	1·56042	127·49
4.	1·77348	1·48110	127·49
5.	2·31048	1·92938	127·44
6.	2·14267	1·78936	127·50
7.	2·35523	1·96676	127·45
8.	2·18860	1·82780	127·54
9.	3·29158	2·74881	127·50
10.	2·27516	1·89993	127·46
11.	2·53164	2·11410	127·46
12.	2·01327	1·68121	127·45
		Average	127·48

In the second and third columns are given the apparent weights of the nitrate and oxide. In calculating the values of the atomic weight, a vacuum correction was made of +0·150 mgrm. for each grm. of nitrate and +0·066 mgrm. for each grm. of oxide. The specific gravity of tellurium dioxide has been reported as 5·76. The value of this con-

stant for the basic nitrate of tellurium was found to be 4·26 at 22°/4°. The atomic weights used in the calculation were H, 1·0076; N, 14·01; O, 16.

When the results are calculated in the manner used by Köthner,—namely, H, 1·01; N, 14·04; O, 16,—and no vacuum corrections are applied, the average is 127·64. Kothner's average is 127·63.

The results given under Nos. 1, 2, and 3 were those obtained with a sample of nitrate which had been purified by crystallisation only. In the paper by Norris, Fay, and Edgerly it was stated that crystallisation of the basic nitrate served to purify it from all other metals. These results confirm that statement. Köthner showed by a spectroscopic examination that the nitrate prepared by him contained silver and gold. When he determined the atomic weight of tellurium, using a sample of nitrate made from the metal which had not been distilled, he obtained as the atomic weight the value 127·36, which differed by 0·27 unit from the value found when distilled tellurium was used. He considered the cause of this difference to be the presence of silver and gold in the nitrate which was prepared from undistilled tellurium. The results given above, which were obtained with a sample of nitrate which had been purified by crystallisation alone, are practically identical with those obtained from a sample of nitrate prepared from the oxide which had been five times distilled.

The results obtained with the nitrate prepared from the tellurium which had been converted into the telluropentathionate are recorded in experiments numbered 4, 5, and 6. In the experiment numbered 7 the nitrate used was prepared from a sample of oxide which had been distilled but once, while in experiments 8 and 9 the oxide from which the nitrate was made had been distilled five times. In Nos. 10, 11, and 12 are recorded the results of the analyses of samples of nitrate prepared from the residue from the first distillation. If the dvitellurium of Mendeleeff had been present, the atomic weight of this fraction should have been much higher than 127·48.

The results show clearly that the application of the methods studied effected no decomposition of tellurium. As these methods would have shown the presence of an unknown element with the properties which have been assigned to dvitellurium by Mendeleeff, the conclusion can be drawn that no such element is present. The work adds to the experimental evidence in favour of the elementary nature of tellurium.

The atomic weight found agrees well with the most reliable values which have been determined by others.

PROCEEDINGS OF SOCIETIES.

FARADAY SOCIETY.

Ordinary Meeting, January 15th, 1907.

Sir JOSEPH SWAN, F.R.S., Past President, in the Chair.

MR. E. E. FOURNIER D'ALBE read a paper and opened a general discussion on "*The Application of the Electron Theory to Electrolysis.*" (See CHEMICAL NEWS, vol. xcv., p. 28).

Mr. JOHN G. A. RHODIN considered that the electron theory, like the atomic theory, merely complicated matters and was unnecessary. The conception of infinite divisibility was a necessary one in physics as in mathematics, if our reason was to be satisfied. Both in chemistry and physics we know of mathematical relations only, and hypotheses are only crude images. The ether and electrons were invented because certain phenomena could be the more easily treated mathematically by means of these conceptions. A simple theory of ions was all that was necessary for understanding electrolysis; more hypotheses were not wanted. Existing theories left many well known facts without explanation. He suggested the appointment of an International Committee for generalising existing theories, and making them available to the average intelligence.

Dr. H. BORNS asked whether the Hall effect and the recent experiments of Kaufmann did not throw some doubt on the electron theory. Why were there no free electrons in liquids?

Dr. J. A. HARKER was not clear as to whether the theory supposed atoms to be composed entirely of electrons or whether there was a central nucleus. If the former, one would expect more intermediate formations. He thought the fundamental conceptions of the theory should be made perfectly clear, so that the explanations of various phenomena given by it could be deduced from some simple postulates.

Dr. T. M. LOWRY pointed out that much of the work on hydration asked for by the author had been carried out, among others, by Biltz, Jones, and Bousfield. The latter had shown, for example, that the chlorine ion attached five water molecules to itself.

Mr. N. T. M. WILSMORE considered that the theory, which looked upon electrons as exerting a sort of osmotic pressure at the surface of an electrode, conceived admirably the mechanism of electrode potential and of electrode reactions. It was noteworthy that the more electropositive a metal, the more easily it threw off electrons under the stimulus of ultra-violet light, for example. He showed how the theory explained, in a simple manner, oxidation and reduction phenomena, and the action on the positive accumulator plate. He thought that the negative electron should have a distinctive name, and proposed using the word "negatron," which had been suggested.

Mr. F. KAYE remarked on the simple explanation of the different mobilities and therefore hydrations of the various ions on the view that the positive and negative ions acted to different degrees as condensation nuclei. He asked whether when a liquid was evaporated there was a movement of electrons into the vapour.

Mr. F. S. SPIERS pointed out that the theory did not seem to help in explaining the fundamental preliminary to electrolysis, namely, dissociation in solution.

Mr. E. E. FOURNIER D'ALBE replied to the various speakers. He did not think that the few considerations put forward by Mr. Rhodin overthrew the theory. The difficulty of the Hall effect mentioned by Dr. Borns was more serious, but the negative swing that had been observed might be due to positive ions of great mobility, and not necessarily to the existence of positive electrons. A similar recent observation of the Faraday effect could be similarly explained. Kaufmann's experiments dealt with structure of electrons and merely pointed to Abraham's theory of a rigid electron being more probable than Lorentz's, which, in order to account for the Michelson-Morley experiments, supposed the electron to become shortened in its passage through the ether. Their great mobility in face of little resistance would prevent free electrons existing in liquids. When a metal was liquefied, probably polymerisation took place, and ions were formed which carried the current.

In reply to Dr. Harker, it seemed that atoms most likely consisted of negative electrons whirling round a positive nucleus. The solar system presented a close analogy. Only certain configurations would be stable; hence every intermediate stage of element would not persist. The theory at present could not be built up from simple postulates; it was in the induction stage, and kept in close contact with facts.

In reply to Mr. Kaye, electrons did not pass into the vapour from a boiling liquid; the surface of the liquid was a perfect semi-permeable membrane.

The CHAIRMAN, in moving a vote of thanks to the author for his important and interesting paper, which had stood so well the trying ordeal of some trenchant criticism, referred to the inadequacy of the old ideas to account completely for all the phenomena of conduction,

electrolytic and other, ideas which he none the less found it not easy to get rid of, without at least some further consideration.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 2, January 14, 1907.

Apparatus for the Preparation of Pure Oxygen Utilisable in Organic Analysis.—A. Seyewetz and M. Poizat.—This is a method for producing a continuous supply of pure oxygen under a pressure sufficiently constant to admit of its taking the place of a gasometer. The method turns upon the reaction of permanganate of potassium with hydrogen peroxide. After operating in acid, neutral, and alkaline solution respectively, it was found that in the acid medium the best results were obtained. Whether the hydrogen peroxide was allowed to drop into the solution of permanganate or *vice versâ* was found to be immaterial, but it was an indispensable condition that the solution which dropped into the other should be the denser; otherwise the two liquids did not mix or react well together. This condition is always fulfilled by mixing the acid necessary to the reaction with the flowing solution. About 10 litres of oxygen were thus obtained for 500 cc. of water oxidised to ten volumes. The only impurities contained in the oxygen were traces of chlorine and ozone. The chlorine was removed by passing the gas through potash solution. The authors found that the use of this apparatus gave excellent results in connection with organic combustions, making the use of a gasometer quite dispensable.

A Case of Isomerism in the Oxygen Combinations of Grignard and Baeyer.—W. Tschelinzeff.—There are two different structures attributed to the complex molecules formed by ether and the organo-magnesium compounds, one of which $\frac{R}{R}>O<\frac{X}{MgR}$, was proposed by Baeyer, and the other, $\frac{R}{R}>O<\frac{R}{MgX}$, by Grignard. The author affirms that most of the observed facts point to the former as being the correct structure, *e.g.*, from the analogies presented by these bodies with ammoniacal compounds, and the combinations formed by the action of the ethers upon the halogen acids, as well as their peculiar activity in relation to different carboxyl combinations having the same radical as the iodide. Baeyer's interpretation admits of possible interesting isomers theoretically, such as the following :— $\frac{R}{R}>O<\frac{X}{MgR'}$ and $\frac{R'}{R}>O<\frac{X}{MgR}$, which would not be distinct bodies according to Grignard's arrangement. From experiments on the decomposition of these substances by water the presence of an isomer is demonstrated. The author has investigated thermochemically the decomposition by water of certain of those combinations as a means of determining the influence exerted by the position of the radical upon the bonds uniting the atoms. The results of the researches showed that the thermal effects differed too slightly for any conclusion to be formulated from them as to the isomerism of bodies in question; but it was proved beyond doubt that the ether-organo-magnesium compounds are manifested in isomeric forms, according to the nature of the bodies serving as the point of departure.

The Superoxide of Methylethylketone. — M. Pastureau.—For acetones of the fatty series it is a general fact that hydrogen peroxide, in presence of an acid catalyser, gives with dimethylketone a superoxide, $(C_3H_6O_2)_2$, and an acetone-alcohol, the acetol $C_3H_6O_2$. The author has isolated the superoxide $(C_4H_8O_2)_2$ from the methylacetol, or acetylmethylcarbinol, $C_4H_8O_2$, produced by the action of hydrogen peroxide upon methylethylketone in presence of sulphuric acid. The superoxide is an oily colourless liquid, of agreeable odour, quite stable at the ordinary temperature, but explosive when heated above 100°; insoluble in water, soluble in alcohol, ether, and benzene; density at 15°, 1·042. *Analysis.*— Found (per cent)—C, 54·2; H, 9·4. Calculated for $C_4H_8O_2$ (per cent)—C, 54·54; H, 9·09. The molecular weight, determined by the cryoscopic method with benzene as solvent, corresponds to the formula $(C_4H_8O_2)_2$. Its chemical properties are those of a superoxide.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxix., No. 17, 1906.

Colbatic Molybdates.—Carl Friedheim and F. Keller.—The cobaltic molybdates, unlike the similar cobaltous compounds, give off chlorine when boiled with hydrochloric acid. They are green in colour, and are formed when mixtures of cobaltous acetate and ammonium or potassium paramolybdate, $3R_2O.7MoO_3$, are treated with persulphate or hydrogen peroxide, or when ammonium permolybdate, $3(NH_4)_2O.5MoO_3.2MoO_4.6H_2O$, acts on cobaltous acetate. Generally speaking, the solutions are mixed in the cold and then more or less strongly heated. The colour then changes from pink to green, oxygen escapes, and some insoluble cobaltous molybdate separates out, while the cobaltic molybdate can be obtained from the liquid by crystallisation. The compounds which the authors have prepared are :—

$3BaO.CoO.CoO_2.9MoO_3$,
$2(NH_4)_2O.CoO.CoO_2.10MoO_3$.
$2BaO.CoO.CoO_2.10MoO_3$.
$3K_2O.CoO.CoO_2.10MoO_3$.
$3(NH_4)_2O.CoO.CoO_2.12MoO_3$.
$3K_2O.CoO.CoO_2.12MoO_3$.

Preparation and Properties of Antimony Pentafluoride.—Otto Ruff.—Hydrofluoric acid is condensed by a good cooling mixture in a platinum retort, and cooled antimony pentachloride is added, taking special precautions to ensure the presence of a large excess of the acid. This is necessary because the antimony pentafluoride formed gives a fluorhydrate with hydrofluoric acid, and this reacts much more slowly with the pentachloride, and is only decomposed into its constituents at a high temperature. The hydrofluoric acid must be completely removed before the antimony pentafluoride can be distilled off. Moreover, the yield may be greatly affected by the presence of potassium fluoride in the acid, which must therefore be first purified. As regards the chemical properties of the pentafluoride, with chlorine it gives no fluorine; with bromine it gives a tarry dark brown mass, which contains a compound SbF_5Br; with iodine it yields $(SbF_5)_2I$ and SbF_5I; with sulphur it forms a blue solution from which SbF_5S can be isolated. It is indifferent towards most dry metals, and in dry air and in dry carbon dioxide it sublimes without leaving any residue. On the addition of water it passes over into the solid hydrate, $SbF_5.2H_2O$, and with more water it gives a clear solution which is not decomposed on boiling. The solution, when mixed with sodium carbonate or caustic soda solution, yields acid sodium pyrantimoniate quantitatively. When the aqueous solution is evaporated a hydrate of antimony pentafluoride is first left, and after heating *in vacuo* this leaves, finally, antimonic acid. In a current of sulphuretted hydrogen, sulphur, hydrofluoric acid, antimony sulphofluoride and antimony trifluoride are formed. The author has also investigated its behaviour with many other inorganic and organic compounds. Of the latter, wood, cork, and rubber are all strongly attacked; benzene and ether react with it vigorously, and carbon tetrachloride yields CCl_3F. When the actions of the halogens and sulphur on antimony pentafluoride were examined quantitatively, it was found that it reacted most

vigorously with chlorine, and then with bromine, iodine, and sulphur in the order as given. With antimony trifluoride it forms stable compounds of the empirical composition $SbF_5.2SbF_3$ to $SbF_5.5SbF_3$. When dry ammonia gas is led over SbF_5 a reaction occurs, and much heat is evolved. The pentafluoride becomes covered with a thick yellowish red incrustation, which soon stops further action. The effect of liquid ammonia was therefore investigated, and a new compound was thus isolated. It has the formula $SbF_3.(NH_2)_4$ or $Sb_2F_8.(NH_2)_3$, and is the difluorhydrate of diamidodiantimony fluorimide. The boiling-point of antimony pentafluoride the author finds to be 149—150°.

Violet and Green Chromium Chloride.—F. Jost.—The author has determined the position of the six molecules of water in the chromium chlorides by finding the properties of the salts in a solvent in which there can be no doubt about the method of combination of the water. He chose methyl alcohol as solvent, and measured the lowering of the tension and the conductivity of the two salts. His experiments prove that in the green hydrate the water is more loosely held, for a lowering of the tension was found, which shows that on dissolving a molecule of the green hydrate eight active molecules are formed in the solution, while with the violet salt only four or five are formed, although the number of ions is less in the former case. In both cases the lowering of the tension was greater than was to be expected according to Werner's co-ordination formulæ :—

$[Cr(OH_2)_6]Cl_3$ — Violet chloride.

$\left[Cr\begin{matrix}(OH_2)_4\\Cl_2\end{matrix}\right]Cl.$ — Green chloride.

This is to be explained by supposing that even in the nucleus water molecules are replaced by the molecules of the solvent. On evaporating the solution in methyl alcohol the salts would not crystallise out again.

New Method of Reduction (I.).—Th. Weyl.—Pure red phosphorus on being boiled with water or alkali gives large quantities of phosphoretted hydrogen. This is also the case when acids, *e.g.*, hydrochloric or sulphuric acid, act upon red phosphorus, and, moreover, the nascent PH_3 thus evolved may be used as a reducing agent. Its action was investigated quantitatively by allowing red phosphorus and water to act upon nitrobenzene in a closed vessel at 100°. The aniline thus formed was then determined; it amounted to 86 per cent of the theoretical yield, under favourable conditions. Apparently in the first stage of the reaction phosphoretted hydrogen results, and then reduces the nitro-group as shown by the equation $3C_6H_5.NO_2 + 4PH_3 \rightarrow 3C_6H_5NH_2 + 2H_3PO_3 + 2P$. In the second stage the phosphorus which separates yields fresh PH_3 with the water, and this then reduces a further quantity of nitrobenzene. According to the equation, roughly, 35 grms. of phosphorus would be required for the reduction of 100 grms. of nitrobenzene, and half of it, viz., 17·5 grms., would be recovered. But the great excess of water attacks the unused phosphorus according to the equation $4P + 6H_2O = 3H_3PO_2 + PH_3$, and secondary reactions also occur.

Reduction of Nitrobenzene by Aliphatic Alcohols in Light.—Giacomo Ciamician and P. Silber.—It is known that nitrobenzene is reduced by a fatty alcohol (not methyl) according to the following scheme :— $C_6H_5.NO_2 \rightarrow C_6H_5.NH.OH \rightarrow C_6H_5NH_2$. As to the fate of the alcohol it was supposed that it formed the corresponding aldehyde and then combined with the aniline to form the corresponding quinoline bases, which are found in the products of the reaction. To show that these quinoline bases are not formed from the aniline by the action of light, a mixture of aniline and paraldehyde was exposed to light for a year, when it was found that the product consisted almost entirely of aniline picrate.

Cuprous Sulphate.—F. Foerster and F. Blankenberg.—It is known that copper is taken up by cupric sulphate solution yielding cuprous sulphate, until equilibrium ensues, as shown by the equation $2Cu^{\cdot} \rightleftarrows Cu^{\cdot\cdot} + Cu$. According to this, by the law of mass action at a given temperature, $\frac{(C_{Cu^{\cdot}})^2}{C_{Cu^{\cdot\cdot}}} = \text{constant}$. If it is assumed that the cuprous sulphate is completely dissociated, and the cupric sulphate is 17 per cent dissociated, the value of this constant is $0{\cdot}66 \times 10^{-2}$. Its value increases as the temperature rises. This holds for an acid solution. In solutions free from acid the formation of the cuprous salt is somewhat favoured by the great inclination of cuprous sulphate to undergo hydrolysis with separation of cuprous oxide :— $Cu_2SO_4 + H_2O \rightleftarrows Cu_2O + H_2SO_4$. The solution, however, is thus made acid, and the hydrolysis is finally stopped. The formula shows that as the concentration of the cupric salt increases that of the cuprous salt increases too. But as it is the second power of the cuprous ions which is proportional to the first power of the cupric ions, it follows that at a given temperature the total amount of copper ions present is greater the smaller the concentration of the copper ions in the solution. Thus, if we start with a complex cupric solution, the cuprous salt must be correspondingly concentrated. The ammonia compounds are very suitable to use to investigate this point. The authors have studied the effects of introducing ammonium cupric sulphate solution and copper-wire into glass tubes which are afterwards fused up, and has determined the point at which equilibrium ensues by immersing a platinum-foil as cathode, and copper-wire as anode, and passing a current through. Copper is separated owing to the two processes $Cu^{\cdot} \cdot O \rightarrow Cu$ and $Cu^{\cdot\cdot} + 2O \rightarrow Cu$. If far more copper is separated by the current than in a coulometer in which the process $Cu^{\cdot\cdot} + 2O \rightarrow Cu$ is proceeding, it shows that equilibrium has been reached. In the course of these experiments the authors have succeeded in obtaining crystalline cuprous sulphate in the form of an ammonia compound; the formula is $Cu_2SO_4.4NH_3.H_2O$. The salt is unstable, but when quite dry can be kept for some weeks in fused-up tubes at the ordinary temperature. With dilute sulphuric acid the crystals turn bright red, and give metallic copper and cupric salt. Possibly the other oxygen salts of the cuprous series can be crystallised in the form of ammonia compounds, and the authors have already obtained a crystalline compound of cuprous chloride with ammonia.

MISCELLANEOUS.

Institute of Chemistry.—*Past List of the January Examinations, 1907.*—Of eleven candidates who entered for the Intermediate Examination the following eight passed :—R. R. Bennett, A. G. Harrington, J. H. Lane, C. P. Matthews, B.Sc. (Lond.), A. Miller, M.B. (Lond.), Capt. I.M.S., P. Murphy, B. D. Porritt, and E. C. Ward. In the Final Examination for the Associateship (A.I.C.), of seven examined in the branch of Mineral Chemistry five passed—J. Dick, jun., C. M. W. Grieb, B.Sc. (Lond.), A. T. King, B.Sc. (Lond.), A. Lathwood, B.Sc. (Lond.), and J. F. Reid; of three examined in Metallurgical Chemistry two passed—H. G. Dale and R. F. Innes; of three in the branch of Organic Chemistry one passed—H. Stanley, B.Sc. (Lond.); and of ten (including one Associate) who entered in the branch of the Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following eight passed—T. R. Hodgson, B.A. (Cantab.), H. Hurst, B. R. James, J. D. Kettle, B.Sc. (Lond.), F. Maudsley, B.Sc. (Vict.), J. Thompson, Ph.D. (Heidelberg), W. A. Whatmough, A.I.C., and C. H. Wright, B.A. (Cantab.). The Examiners in Chemistry were Mr. W. W. Fisher, M.A. (Oxon.), F.I.C., and Dr. G. G. Henderson, M.A. (Glasgow), F.I.C. The Examination in Therapeutics, Pharmacology, and Microscopy was conducted by Dr. F. Gowland Hopkins, M.A. (Cantab.), F.R.S., F.I.C.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Society of Arts, 8. (Cantor Lectures). "Gold Mining and Gold Production," by J. W. Gregory.
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Chemical Composition of some Motor Tyre Rubbers" and "Composition of some New Crude Rubbers," by P. Schidrowitz and F. Kaye.

TUESDAY, 5th.—Royal Institution, 3. "Survivals from the Past in the Plant World," by Prof. A. C. Seward, F.R.S.

WEDNESDAY, 6th.—Society of Public Analysts, 8.15. (Annual General Meeting). "Mineral Acids in Vinegar" and "Composition of English Fermentation Vinegar," by F. D. Ratcliff. "Detection of Cane-sugar in Milk," by W. H. Anderson.
—— Society of Arts, 8. "The Principles and Practice of Insurance, and their Modern Developments," by Thomas Emley Young, B.A.

THURSDAY, 7th.—Royal Institution, 3. "Standards of Weights and Measures," by Major Percy A. Macmahon, F.R.S.
—— Chemical, 8.30. "Rapid Electro-analytical Deposition and Separation of Metals—Part I, The Metals of the Silver and Copper Groups and Zinc," by H. J. S. Sand. "The Alkaloids of Ergot," by G. Barger and F. H. Carr. "Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds—Part VI., The Partially Methylated 4 : 6-Diamino-*m*-xylenes," by G. T. Morgan and F. M. G. Micklethwait. "Reduction of Hydroxylaminodihydrocumbellulone Oxime" and "The Constitution of Umbellulone —Part II., Reduction of Umbellulonic Acid," by F. Tutin. "Studies on Optically Active Carbimides—Part V., The Aryl Esters and the Amides of *l*-Menthylcarbamic Acid," by R. H. Pickard and W. Oswald. "Some Constituents of Natural Indigo," by A. G. Perkin and W. P. Bloxam. "Occurrence of Isatin in some Samples of Java Indigo," by A. G. Perkin. "Absorption Spectra of Benzoic Acid, the Benzoates, and Benzamide" and "Absorption Spectra of Phthalic, Isophthalic, and Terephthalic Acids—Phthalic Anhydride and Phthalimide," by W. N. Hartley and E. P. Hedley. $\alpha\alpha\gamma$-Trimethyl- and $\alpha\alpha\gamma\gamma$-Tetramethyl-tricarballylic Acids and $\alpha\Delta$-Dimethyl-butane $\alpha\beta\Delta$-Tricarboxylic Acid," by H. Henstock and C. H. G. Spranking. "Reaction of certain Colouring-matters of the Oxazine Series," by J. F. Thorpe.

FRIDAY, 8th.—Royal Institution, 9. "Old English Poetry," by Prof. I. Gollancz, M.A., Litt.D.
—— Physical, 8. (Annual General Meeting). President's Address. "The Magnetic Fields and Inductive Coefficients of Circular, Cylindrical, and Helical Currents," by A. Russell.

SATURDAY, 9th.—Royal Institution, 3. "Papal Deposing Power," by the Rev. William Barry, D.D.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2463.

BORIC ACID: ITS DETECTION AND DETERMINATION IN LARGE OR SMALL AMOUNTS.*

By WILSON H. LOW.

(Continued from p. 51).

Quantitative Test.

The limit of the test, as here arranged, is one drop or 0·05 cc. of N/10 sodium hydroxide solution. This corresponds to 0·00031 grm. of boric acid or 0·00062 per cent, or about 0·10 ounce per 100 pounds of the food product, a quantity absurdly small for any preservative effect.

The sample of meat or other food product is ground up or hashed, and 50 grms. of the well-mixed sample taken and placed in a clean cover of a three-pound lard pail, or other similar dish. Spread the meat in a layer over the dish and moisten with 25 cc. of N/1 sodium carbonate solution, or equivalent, and dry on the steam-bath, oven, or electric stove. It is a great advantage to dry before igniting, as by so doing the meat does not swell up, and burns off much easier. The quantity of sodium carbonate directed to be added is more than sufficient to retain 1 per cent of boric acid, and this is more than would be used. 25 cc. of N/2 sodium carbonate are generally sufficient, and makes the burning to carbonaceous ash quicker. Ignite gently, heating the whole bottom of the dish, if possible, to a carbonaceous ash free from brown products soluble in water. Do not burn off all the carbon. Allow to cool, and with a spatula scrape out the ash into a smooth mortar (a glass mortar is best). Grind up fairly fine and transfer from the mortar to the distillation flask. This is easily done, as the smooth mortar allows the ash to slide out completely. Put about 10 cc. of water into the dish from which the ash was scraped, add 1 cc. of strong hydrochloric acid, and allow to act about thirty seconds (we want to avoid dissolving the iron to any extent), and then pour into the distillation flask. This will sufficiently wash out the dish, and there would be no particular loss if this step was left out. About 3 to 5 cc. of strong hydrochloric acid are added to the distillation flask, and the ash allowed to soak in the liquid for a few minutes to dissolve as much as possible, the object being to get all the boric acid in solution. Ten to 15 grms. of dry, granulated, chemically pure calcium chloride are now added, and allowed to dissolve as much as will in a few minutes' shaking. Connect up the flask in its place in the distillation system and pass methyl alcohol vapour through. Usually no attempt is made to heat this flask except by the methyl alcohol vapour itself, but there is no harm in so doing after 50 to 100 cc. of the alcohol have condensed in it. When about 100 cc. of distillate has been obtained it is drawn off and tested. The distillation is allowed to go on without interruption, and each 100 cc. or less are drawn off and tested till no more boric acid is found. When the last distillate gives a test requiring only one drop of N/10 sodium hydroxide solution the process is generally assumed finished, as without great care the blank test on the glycerol alone or in the presence of salts will vary a drop. If necessary the determination can be made absolutely to within one drop of N/10 sodium hydroxide.

Each distillate is tested as follows:—It is drawn off into a flask similar to the distillation flask (a round-bottomed flask holding up to the neck about 275 cc.), and one drop of nitrophenol indicator solution added. N/1 sodium hydroxide solution is dropped in till the yellow colour of the indicator is seen. Practically all the mineral acid that has distilled over is now neutralised. Experiment shows that very little mineral acid does distil over, even with a large excess in the distillation flask, unless the contents of the distillation flask are concentrated. Now add about 1 cc. of the phenolphthalein indicator and run in N/1 sodium hydroxide solution till the pink colour is seen. As soon as you are sure the coloration is reddish or pink, that will do without making it strong. The difference between the end-points with nitrophenol and phenolphthalein will be a close measure of the boric acid present, as the methyl alcohol takes the part of glycerol, and would probably be just as good as the latter but for its peculiar effect on some indicators. After finding how many cubic centimetres correspond to the boric acid, add twice as much more alkali; that is, if the difference in end-points between nitrophenol and phenolphthalein was 10 cc. then add 20 cc. more of the alkali. This is to ensure enough alkali to combine with the boric acid to form Na_3BO_3, which is certainly enough to prevent loss of boric acid on evaporating off the methyl alcohol. In all probability this is more than enough. The compound or mixture of boric acid and alkali that is stable in boiling methyl alcohol is stated by E. Polenske (*Journ. Soc. Chem. Ind.*, 1901, xx., 273) to have the composition $5Na_2O.4B_2O_3$, and this is apparently a mixture of $NaBO_2$ and Na_2O. Now put a capillary boiling tube into the flask and evaporate off the methyl alcohol on the steam-bath. When the alcohol has evaporated, dissolve the residue in about 25 cc. of water, and run in N/1 sulphuric acid till the solution is colourless. If a large quantity of N/1 sodium hydroxide solution has been used, necessitating a large quantity of acid, it is better to drop in strong hydrochloric acid till the solution is colourless, thus keeping the bulk down. Next, holding the neck of the flask with a clamp, put the flask into the steam-bath for a few minutes, take out and quickly connect with the suction pump (a large-sized Chapman is very good). The flask will be rapidly exhausted, and the solution will boil vigorously and all carbon dioxide will be expelled. The evaporation cools the contents of the flask rapidly, and if there is any doubt that all carbon dioxide has been expelled, the heating and boiling may be repeated, as there is no fear of losing boric acid, except mechanically. Note that the solution should be colourless when hot as well as when cold; if not, add more acid and heat again. Sometimes the yellow colour of the nitrophenol is seen in the hot liquid, due to the decomposition of the bicarbonates and showing that not enough acid has been added. The phenolphthalein indicator will often separate out as an insoluble white precipitate as the solution cools. This is of no particular consequence as it clears up again later, and experiments seem to indicate that 1 cc. of this indicator solution is better to use than a smaller quantity. The solution is now cold and free from carbon dioxide. Break the vacuum and run in N/1 sodium hydroxide solution till the last drop turns the nitrophenol indicator yellow. Now run back to acid reaction with one drop of N/1 sulphuric acid, and then run to just alkaline reaction with N/10 sodium hydroxide. In some cases in running to alkaline reaction with N/10 sodium hydroxide solution, the yellow colour is very faint (due to large amounts of salts present, or possibly to carbon dioxide not previously expelled), but usually it is well marked. At any rate run to the first point that you are sure is yellowish. Now take 40 cc. of strong glycerol in the 50 cc. graduated cylinder and pour it into the flask, rotating the latter to mix the contents. About 35 cc. of glycerol will flow out with moderate draining. The titration with N/10 or N/1 sodium hydroxide solution (depending on how large a quantity of boric acid is present, and the titration in methyl alcohol has indicated this) is proceeded with till the last drop gives a decided colour change to a reddish or pinkish shade. It is not necessary to run to a decided pink colour, as one drop of N/10 sodium hydroxide solution in excess makes a decided

* From the *Journal of the American Chemical Society*, xxviii., No. 7.

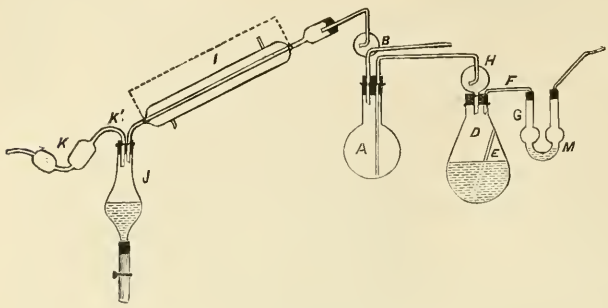


FIG. 1.

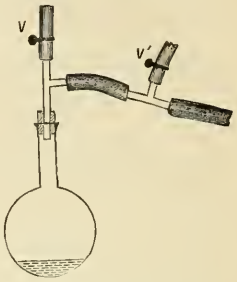


FIG. 2.

A, distillation flask. Capacity about 275 cc. Rests in asbestos cloth on retort stand ring.

B, splash trap, about 5 cm. in diameter. From top of flask to top of bend is about 12 cm.

C, vapour tube. Internal diameter about 4 mm., and at end inside the flask 2½ mm.; this tube must not have too small an opening in the flask on account of danger of becoming clogged.

D, flask made from an 800 cc. Jena glass Kjeldahl digestion flask, cut off as shown. The methyl alcohol is boiled in this flask. It is furnished with the absolutely necessary boiling tube E.

E, boiling tube, about 16 cm. long, with a capillary bore. About 1 cm. from the end in the alcohol it is sealed. Without this tube the alcohol on boiling bumps fearfully, and would endanger the apparatus and operator. With this tube the boiling is easy, uniform, and without danger. It is necessary to shake out the alcohol from the capillary and put it back into the alcohol each time the solution is started boiling.

F, bend and rubber tube connecting the boiling flask with the small safety U-tube.

G, U-tube of small size containing a little mercury in the bend. This acts as a safety-valve in case the apparatus gets clogged, and prevents the blowing out of the stopper from the boiling flask. A long tube leads from the U-tube to carry off the alcohol vapour should it blow out. The rubber tube should slope towards the boiling flask.

H is a splash trap, the same as B, except that the tube leads from it at right angles. It is connected with C by a sliding piece of rubber tubing.

I is the condenser, about 38 cm. long between the dotted lines and about 50 cm. over all.

J is the collecting flask. Mine is made by blowing out the bottom of a 200 cc. Erlenmeyer flask and drawing down to a tube. It is furnished with a rubber tube and pinch-cock at the bottom.

K is the absorption tube with the water seal, to prevent loss of methyl borate. At the end of each 100 cc. of distillate, the contents of this tube are run into the distillate taken off. K' = rubber connection.

Flask connected to vacuum pump VV' (Fig. 2) are T-tubes and rubber tubing with screw pinch-cocks. The vacuum should always be broken by opening cock V to prevent any possible return of condensed water.

change from the strong yellow of the nitrophenol to a colour with a reddish tint due to phenolphthalein. The progress of the titration is well seen in the change of depth of colour due to nitrophenol. As the end-point is approached the yellow colour grows very intense. The difference between the end-point to nitrophenol and phenolphthalein multiplied by 0·0062024 gives the grms. of boric acid, if N/10 alkali has been used in the titration. Each 100 cc. of distillate, or whatever quantity is drawn off each time, is tested in this way. A blank had best be run by taking 10 cc. of N/1 sodium hydroxide solution, adding a slight excess of N/1 sulphuric acid, and about 10 cc. of water, and boiling under vacuum as in the test, and then bringing to just alkaline reaction to nitrophenol with N/10 sodium hydroxide solution, adding the same amount of glycerol and titrating to the end-point with phenolphthalein indicator.

There need be no mistaking the end-points, and test experiments have shown that nitrophenol gives the same end-point as methyl orange (first noticeable change), and is greatly to be preferred, as there is no change through several shades to the end as there is with methyl-orange. However, methyl-orange may be used with equal accuracy, paying due attention to running to the same shade of end-point each time. An exception must be made to the last statement in regard to the preliminary titration of the boric acid when in methyl alcohol solution. Methyl-orange here is of no value. If for any reason it is found necessary to use more than 10 cc. of water and 5 cc. of hydrochloric acid in the distillation flask, it will be necessary to increase the amount of calcium chloride to take care of the additional water. Use about two-thirds of a grm. of calcium chloride to 1 cc. of the aqueous solution in the distillation flask. The idea is to have all the boric acid in solution, as then it is quickly volatilised. The arrangement of the apparatus will be seen from the sketch.

(To be continued).

Royal Institution.—On Tuesday next, February 12, at 3 o'clock, Professor William Stirling begins a course of six lectures at the Royal Institution on "The Visual Apparatus of Man and Animals"; on Thursday, February 14, at the same hour, Mr. A. Harker gives the first of two lectures on "The Minute Structures of Igneous Rocks and their Significance"; and on Saturday, February 16, also at 3 o'clock, Professor J. J. Thomson commences a course of six lectures on "Röntgen, Cathode, and Positive Rays." The Friday Evening Discourse on February 8 will be delivered by Professor I. Gollancz on "Old English Poetry," and on February 15 by Mr. J. J. Lister on "Foraminifera."

THE

CARRYING DOWN OF AMMONIUM OXALATE BY OXALATES OF THE RARE EARTHS.*

By GREGORY PAUL BAXTER and ROGER CASTLE GRIFFIN.

A RAPID and convenient method for approximate atomic weight determinations of the trivalent metals of the rare earths is the "permanganate" method, in which the ratio $M_2O_3 : 3C_2O_3$ is determined. In this process a known weight of the oxalate of the rare earth is ignited to oxide and the latter is weighed. Then a known weight of the same sample of oxalate is dissolved in sulphuric acid, and the oxalic acid is titrated with standard potassium permanganate. By dividing the ratio $\frac{M_2O_3}{M_2(C_2O_4)_3}$ found in the first process by the ratio $\frac{3C_2O_3}{M_2(C_2O_4)_3}$ found in the second, the ratio $\frac{M_2O_3}{3C_2O_3}$ is determined, from which the atomic weight may be calculated. (This method was first proposed by Stolba, *Sitzber. Böhm. Ges.*, Dec., 1878; also CHEMICAL NEWS, 1880, xli., 31).

It has already been pointed out by Gibbs (*Proc. Am. Acad.*, 1893, xxviii., 262) and others that the oxalates of the rare earths contain varying amounts of water, and that it is very necessary to grind thoroughly the whole specimen of oxalate which is to be used for analytical purposes, in order to ensure homogeneity of material. Furthermore, the fact has long been recognised that in the presence of potassium or sodium oxalates some of these substances may be carried down by the insoluble oxalates. Large discrepancies in the observed atomic weight as determined by the above method, with material which had been precipitated by oxalic acid or ammonium oxalate, led to the following research upon the effect of varying conditions upon the composition of the oxalates of certain of the rare earths. It is found that ammonium oxalate also, but not oxalic acid, may be carried down in considerable quantities by the rare earth oxalates.

Neodymium was the first element studied. A specimen of oxalate was ignited to oxide, and dissolved in a considerable excess of nitric acid. The absorption spectrum of the solution showed the bands of neodymium only. A portion of the solution was then slowly added, with constant stirring, to a solution of a large excess of oxalic acid. The resulting oxalate was washed ten times by decantation with hot water, and collected on a porcelain Gooch crucible, provided with a disk of filter-paper instead of asbestos. On testing the filtrate the precipitation of the neodymium was found to be complete. After the oxalate had been dried in an electric air-bath at 120—130° for about twenty hours, it was thoroughly mixed by grinding in a porcelain mortar.

Portions of about 0·5 grm. were then transferred from a weighing-bottle to weighed platinum crucibles, and the crucibles were ignited, first in a Bunsen flame, and finally for several minutes with a blast-lamp. The crucibles were allowed to cool in desiccators, and were again weighed. In each case a repetition of the ignition failed to change the weight of the oxide.

Next, portions of from 0·2 to 0·3 of a grm. of the oxalate were weighed into Erlenmeyer flasks, and after the addition of about 5 cc. of concentrated sulphuric acid diluted with 50 of water, the flasks were heated an the steam-bath until the oxalate was completely dissolved. Then the oxalic acid was determined by titration with potassium permanganate solution. This solution was standardised with oxalic acid which had been allowed to come to constancy over sulphuric acid of the sp. gr. 1·35. The oxalic acid had been many times re-crystallised, first from hydrochloric acid solution, then from pure water until free from chlorides.

Since the weight of oxalate found experimentally was considerably less than 100 per cent, as a check on the process the water content was determined by igniting weighed portions of the oxalate in a porcelain boat in a current of dry air, and absorbing the water in a weighed phosphorus pentoxide tube.

The results of the complete analysis are as follows:—

	I.	II.	III.	Average.
Weight of oxalate..	0·6505	0·5938	0·5865	
Weight of Nd_2O_3..	0·3182	0·2908	0·2869	
Per cent of Nd_2O_3 .	48·92	48·97	48·92	48·94
Weight of oxalate..	0·3164	0·3230	0·2613	
Vol. of $KMnO_4$ sol.	28·03	28·60	23·16	

1 cc. $KMnO_4$ = 0·003547 grm. C_2O_3.

C_2O_3 calculated ..	0·0994	0·1014	0·0822	
Per cent of C_2O_3 ..	31·43	31·41	31·44	31·43
Weight of oxalate..	0·6575	0·6264		
Weight of water ..	0·1278	0·1241		
Per cent of water..	19·44	19·81		19·62
Total..				99·99

$$\text{Ratio, } M_2O_3 : 3C_2O_3 = \frac{48{\cdot}94}{31{\cdot}43} = 1{\cdot}5571$$

$$M = 144{\cdot}2 \quad (Nd = 143{\cdot}6)$$

The observed value for the atomic weight of neodymium is as near the most probable value of this constant as the purity of the sample would lead one to expect. Since the oxalate used in the above experiments was precipitated with a very large excess of oxalic acid, the possibility existed that some of the precipitant had been carried down by the precipitate. In order to determine whether this was the case, another sample of the same material was precipitated in a similar manner, but with a very slight excess of oxalic acid.

	I.	II.	III.	Average.
Per cent of Nd_2O_3..	58·02	57·98	57·94	57·98
Per cent of C_2O_3 ..	37·25	37·27	37·17	37·23

$$\text{Ratio, } M_2O_3 : 3C_2O_3 = \frac{57{\cdot}98}{37{\cdot}23} = 1{\cdot}5573$$

$$M = 144{\cdot}2 \quad (Nd = 143\ 6).$$

The agreement of the values for the atomic weight of neodymium obtained from the analyses of oxalate which had been precipitated with a very large and with a slight excess of oxalic acid shows conclusively that no appreciable tendency for the carrying down of oxalic acid exists.

Precipitation by means of ammonium oxalate was next investigated. A solution of neodymium oxide in nitric acid was nearly neutralised with ammonia, and was added to a slightly ammoniacal solution of a small excess of ammonium oxalate. Precipitation was found to be complete. After the precipitation the supernatant liquid was faintly acid. By adding the neodymium solution to the oxalate, occlusion, if it exists at all, is to be expected to be at a maximum. The oxalate was thoroughly washed, dried, and powdered. Then it was analysed as before.

	I.	II.	III.	Average.
Per cent of Nd_2O_3..	50·65	50·58	50·70	50·64
Per cent of C_2O_3 ..	37·99	38·01	38·02	38·01
Per cent of H_2O ..	11·28	11·22		11·25
Total..				99·90

$$\text{Ratio, } M_2O_3 : 3C_2O_3 = \frac{50{\cdot}64}{38{\cdot}01} = 1{\cdot}3322$$

$$M = 119{\cdot}9 \quad (Nd = 143{\cdot}6)$$

Since it was certain from these results that the salt contained too much oxalate, and since it was probable that the excess was due to ammonium oxalate which had been carried down by the neodymium oxalate, a portion of the precipitate was tested for ammonia, after solution in nitric acid, by adding an excess of potassium hydroxide. Ammonia was evolved in quantity, It was evident, therefore, that ammonium oxalate is carried down by neodymium

* From the *Journal of the American Chemical Society*, xxviii., No. 12.

oxalate to a considerable extent. The determination of the water in this oxalate includes the ammonia as well as the water. However, since ammonium oxalate, when heated breaks up partially into cyanogen and water, this determination is slightly in error. During the analysis of the oxalate for water the odour of cyanogen was perceptible.

(To be continued).

DEATH OF PROFESSOR MENDELEEFF.

Dmitri Ivanovitch Mendeleeff, the greatest chemist whom Russia has produced, died at St. Petersburg on February 2nd, within less than a week of reaching his seventy-third birthday.

He was born at Tobolsk, in Siberia, and was educated at the local gymnasium, of which his father was director; his strong bent for natural science early showing itself, he continued his studies at the University of St. Petersburg, where he obtained the M.A. degree, for which he prepared a dissertation on specific volumes and problems concerning the specific gravities and volumes, and the chemical composition of substances.

In 1861 he published accounts of his investigations of the absolute boiling-points of gases, and his fundamental experiments were afterwards amplified and further explained by Andrews, who called the absolute boiling-point the critical temperature. After graduation Mendeleeff adopted teaching as a profession, and from 1860 to 1863 he resided at Heidelberg, where he directed a private laboratory, afterwards returning to St. Petersburg, first as Professor of Chemistry at the Technological Institute, to become, after three years, Professor at the University, which post he held until 1900, when he was appointed Head of the Standards Department. Soon after he obtained the University Professorship he began to write his "Principles of Chemistry," of which seven editions have appeared in Russian and three in English, while it was translated also into German. The object of this text-book was to "acquaint the student not only with the experimental facts and laws of chemistry, but also with the insight given by this science into the unchangeable substratum underlying the varying forms of matter," and its peculiar value was speedily recognised. The stamp of the author's strong personality is impressed upon every page, and it is undoubtedly one of the most original of text-books, which chains the reader's attention by the vividness of its style and the free use of imagery, which is a distinguishing feature of the philosophical parts of the text. In the later editions Mendeleeff declared himself an opponent of the theory of electrolytic dissociation, which he thought adds nothing to our comprehension of solutions in general, and which he declared does not accord with the observed facts, and he considered also the notion of splitting atoms up into electrons, so far from simplifying our ideas merely complicates them, while he regarded the theory of the transmutation of one element into another as an incorrect deduction due to vague ideas about the nature of the ether, which he could not accept until it had been definitely demonstrated that one element could actually be transformed into another, or matter into ether.

Valuable as the book was, however, as an authoritative text-book of inorganic chemistry, it was most widely known as the work in which was discussed for the first time in detail Mendeleeff's conception of the Periodic Law. Arguing upon the basis that the two signs or manifestations of matter are (1) mass and (2) individuality, and that both matter and the chemical elements are indestructible, he deduced that there must be some bond of union between mass and the chemical elements, and hence also between the properties of an element and its atomic weight. This conception led him to compare the atomic weights and typical properties of the elements, and the result was a paper read before the Russian Chemical Society in March, 1869, entitled "On the Correlation of the Properties and Atomic Weights of the Elements." This paper included practically all the points of the Periodic Law as now generally accepted, and in subsequent articles only further applications of the same principles are to be found.

In his text-book Mendeleeff stated that although when arranging the periodic system he made use of the previous researches of Dumas, Gladstone, and Pettenkofer on the atomic weights of allied elements, he was unacquainted with the work of De Chancourtois and of Newlands, the latter of whom five years previously had called attention to the periodicity of the properties of the elements when arranged in the order of their atomic weights, and had suggested that the unoccupied spaces in the table might be filled by elements then undiscovered, or by known elements whose atomic weights had not been accurately determined. Newlands' work, however, had been received with incredulity and even derision, and it was reserved to Mendeleeff to arouse the genuine interest of the scientific world. This was more particularly due to the fact that he had such a profound belief in the universality of the principle he had enunciated that he did not hesitate to prognosticate from it, and even to correct accepted atomic weights. Thus he foretold not only the existence, but also the general properties and chemical behaviour of new and then undiscovered elements, to fill up blanks in the table he had constructed, and when gallium, scandium, and germanium were isolated it was found that they fulfilled these predictions in a most striking manner, while the existence of the inert gases of the atmosphere had also been foretold from the Law. Moreover, the researches of Roscoe and Zimmermann have shown that he was correct in altering the atomic weight of uranium from 120, which was generally accepted in 1869, to 240, and thus making it correspond with the Periodic System.

It is pleasing to notice that with genuine nobility of mind Mendeleeff recognised that Newlands, De Chancourtois, and Strecker had all independently arrived at the same result, and in the Faraday Lecture delivered by him before the Fellows of the Chemical Society in June, 1889, he said that "they merely wanted the boldness necessary to place the whole question at such a height that its reflection on the facts could be clearly seen," and it is for his intrepidity and the courage of his convictions that he is to be admired, no less than for his remarkable perspicuity.

It was not to be expected that a man of such imagination and daring would, as long as life and strength lasted, cease from putting before the world speculations the truth of which time and research alone could test, and to the present generation he has left as a legacy a hypothesis which is of the most absorbing interest. This is contained in an essay, published in 1902, "An Attempt towards a Chemical Conception of the Ether." Starting with the assumption that the ether possesses both mass and materiality, and by extrapolation inserting a zero group in the Periodic System, and a zero series of elements lighter than hydrogen, he deduced that in this series one element should have an atomic weight many times less than that of hydrogen, *i.e.*, less than 10^{-6} if H = 1; it should have a monatomic molecule like argon and helium, and its exceedingly small density, or, in other words, the exceedingly rapid motion of its molecules, should enable it to permeate and penetrate all matter and space. This gaseous element he believed to be the ether, and he was satisfied that the recently discovered physico-chemical phenomena connected with radio-activity could be satisfactorily explained by assuming the emission of a portion of this ether and the entrance of new ether into the sphere of attraction of particles of normal mean velocity, if it were supposed that uranium and thorium, having the highest atomic weights among the elements, would have in the highest degree that power of attraction which lies between gravity and chemical affinity, and which would cause the accumulation of ether atoms round their molecules. This daring conception of the ether was practically the last product of the brain of the great chemist, and as such is now invested with a peculiar interest for those who are left to lament his loss.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 17th, 1907.

Prof. R. Meldola, F.R.S., President, in the Chair.

Messrs. P. S. Arup, W. C. Ball, and J. Hamer were formally admitted Fellows of the Society.

The President announced the decision of the Council that during the remainder of the present Session the Library shall be kept open for the use of Fellows every Thursday from 10 a.m. until 9 p.m., except on those evenings on which the Society meets, when it will remain open until 10.30 p.m.

Certificates were read for the first time in favour of Messrs. Leslie Hamilton Berry, B.Sc., Penshurst, Croham Park Avenue, S. Croydon; Mohan Nath Kedarnath Dikshit, 21, Burlington Road, Bayswater, W.; John Edwin Farmer, Blelsoe, New Road, Mitcham Junction; Percival John Fryer, 27, Minster Road, Cricklewood, N.W.; William Heber Green, D.Sc., The University, Melbourne; Richard Higham, 133, Mauldeth Road, Withington, Manchester; William James Hoyten, M.R.C.S., F.R.C.P., 37, Ravelstoke Road, Wimbledon Park, S.W.; Francis Townshend Cunynhame Hughes, Major, Royal Mint, Calcutta, India; Sidney James Jennings, B.Sc., 367, Queen's Road, New Cross, S.E.; George Lunan, 50, Garscube Terrace, Murrayfield, Edinburgh; William George Twiney, B.Sc., St. Joseph's College, Colombo, Ceylon; Charles Rowlatt Watkins, B.A., Aldenham School, Elstree, Herts; William Henry Williams, Government Education Dept., Hong Kong.

The Council has ordered the following letter and report to be printed in the *Journal* and *Proceedings* of the Society:—

Government Laboratory,
Clement's Inn Passage, Strand, London, W.C.,
15th November, 1906.

Gentlemen,—I have the honour to forward to you, for presentation to the Council of the Chemical Society, the Report of the International Committee on Atomic Weights, 1907, to which I have affixed, as desired by them, the names of Professors Moissan and Ostwald.

The Committee, for reasons stated in the Report, have suggested new values for the atomic weights of bismuth, nitrogen, tantalum, and terbium, and they are further of opinion that alterations are needed in the atomic weights of silver and chlorine, but before recommending any change as regards these elements they consider it expedient to wait for fuller information of the results of determinations known to be in progress. The new values for silver and chlorine will, of course, have an influence upon a large number of atomic weights.—I am, Gentlemen, Your obedient Servant, T. E. Thorpe.

The Hon. Secretaries, The Chemical Society,
Burlington House, London, W.

Report of the International Committee on Atomic Weights, 1907.

Since the preparation of our last report, for 1906, a number of important memoirs upon atomic weights have appeared. The results obtained may be briefly summarised as follows:—

Bismuth.—Work done at Erlangen under the direction of Gutbier (*Zeit. Elektrochem.*, 1905, xi., 831) has been published in the form of three doctoral dissertations (L. Birckenbach, 1905; H. Mehler, 1905; R. L. Janssen, 1906). Birckenbach, by synthesis of the oxide from the metal, found, in mean, Bi = 208·05. A series of reductions of the oxide gave Bi = 208·08. Mehler determined the ratio $BiBr_3 : AgBr$, and found Bi = 208·05. By synthesis of the sulphate from the metal, Janssen obtained the value Bi = 208·074. These determinations are concordant, and also agree with the earlier measurements by Schneider and Lowe, and with a series by Marignac. The atomic weight of bismuth, therefore, is to be taken as 208·0 in round numbers, and the value 208·5, as hitherto given in our table, is too high.

Bromine.—Baxter's (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1322) determinations of this constant are based upon the antecedent values Ag = 107·93 and Cl = 35·473. Eighteen syntheses of silver bromide gave, in mean, Br = 79·953. Thirteen experiments upon the conversion of AgBr into AgCl gave Br = 79·952.

Cadmium.—The memoir by Baxter, Hines, and Frevert (*Ibid.*, 1906, xxviii., 770) is a continuation of the research which was noted last year. Four ratios were measured with the following results, when Ag = 107·93:—

$CdBr_2 : Ag$	Cd = 112·470
$CdBr_2 : 2AgBr$	Cd = 112·464
$CdCl_2 : 2Ag$	Cd = 112·471
$CdCl_2 : 2AgCl$	Cd = 112·470

Copper.—A series of analyses and syntheses of copper oxide by Murmann (*Monatsh.*, 1906, xxvii., 351) gave the value Cu = 63·53. The data are not concordant, and the determinations are not entitled to much weight.

Iodine.—Gallo (*Gazetta*, 1906, xxxvi., 116) has determined the atomic weight of iodine electrolytically, comparing the iodine liberated by a current with the silver deposited. His values range from 126·82 to 126·98, or, in mean, 126·89 when Ag = 107·93. This result is more nearly in accord with the determination by Stas than with the later measurements.

Nitrogen.—Gray's (*Trans.*, 1905, lxxxvii., 1601) work upon the atomic weight of this element, noticed in our report for 1906, has since been published in full. His mean results are as follows:—From the density of nitric oxide, N = 14·006; from the analysis of nitric oxide N = 14·010; from the density of nitrogen, N = 14·008. The mean of all the determinations is N = 14·0085, or very nearly 14·01. This agrees closely with the earlier measurements by Guye, Rayleigh, and Leduc, and leaves no reasonable doubt but that the new value should replace the 14·04 as given in our annual table. In a later paper (*Trans.*, 1906, lxxxix., 1173) Gray has gathered corroborative evidence from various sources, and has discussed Stas's ratios in order to discover their possible errors. Other discussions of similar purport are by Guye (*Ber.*, 1906, xxxix., 1470; for Guye and Bogdan's complete memoir upon nitrous oxide, see *Journ. Chim. Phys.*, 1905, iii., 537) and Scott (Chemical News, 1906, xciii., 20), but they are not final. Experimental evidence alone can reveal the cause of discrepancy between the new figure and the old.

Palladium.—Amberg (*Annalen*, 1905, cccxli., 235) has re-determined the atomic weight of palladium by analysis of palladosoammine chloride, $PdN_2H_6Cl_2$. The value obtained is Pd = 106·688, or 106·7 nearly. Five other analyses of the same salt, by Krell (*Inaug. Dissertation*, Erlangen, 1906), gave a mean of Pd 106·694. Re-calculated with Richards's value for Cl, and rejecting on experiment as defective, Krell concludes that Pd 106·78 but this again would be lowered by the adoption of the newer value for N. Any change in this constant may well be deferred until the antecedent atomic weights are more definitely known.

Silver.—In an attempt to determine the source of error in Stas's figures for nitrogen, Guye and Ter Gazarian examined the fundamental potassium chlorate ratio (*Comptes Rendus*, 1906, cxliii., 411; see also *Journ. Chim. Phys.*, 1906, iv., 174, for a paper by Guye on the need of a general re-calculation of atomic weights). They found that potassium chlorate crystallises with a small quantity of chloride as an impurity, the amount being nearly constant, and about 2·7 parts in ten thousand. Applying this correction to Stas's ratios, his value for silver is lowered from 107·93 to 107·89. A re-discussion of ten fundamental ratios gave figures for silver ranging from 107·871 to 107·908, or 107·89 in mean. If this conclusion is sus-

tained, the Stas's ratios for silver nitrate will give a value for nitrogen in harmony with the figures obtained by Guye and Gray.

Tantalum.—Hinrichsen and Sahlbom (*Ber.*, 1906, xxxix., 2600) have determined the atomic weight of tantalum by conversion of the metal into the pentoxide. Five such syntheses gave Ta = 180·59 to 181·77, or 181·0 in mean. This value should replace the old determination by Marignac as given in our previous tables.

The Rare Earths.—On the metals of this group a notable amount of work has been published during 1906. From five determinations of water in terbium sulphate, Urbain (*Comptes Rendus*, 1906, cxliii., 957) deduces the value Tb = 159·22; and this should supplant the older, questionable data. In another paper (*Ibid.*, 1906, cxliii., 785) Urbain gives an atomic weight of 163·49 to dysprosium, but without details or weighings.

By a volumetric method, Feit and Przibylla (*Zeit. Anorg. Chem.*, 1906, l., 249) have determined the amount of sulphuric acid required to neutralise several of the oxides in this group, and have in that way obtained new estimates of the corresponding atomic weights. The final results, reduced to a vacuum standard, are as follows:—

Lanthanum	139·17
Praseodymium	140·62
Neodymium	144·52
Samarium	150·47
Europium	152·66
Gadolinium	157·38
Ytterbium	173·52
Yttrium	89·40

In Abegg's "Handbuch der Anorganische Chemie," Brauner has given full summaries of all atomic weight determinations. With these summaries, in connection with the rare earth metals (in Bd. iii., Abth. 1, pp. 263, 276, 284, 304, 318, 335), he has cited some hitherto unpublished determinations of his own. His results are:—

Praseodymium	140·97
Neodymium	143·89
Samarium	150·71
Gadolinium	155·78
Erbium	167·14
Ytterbium	173·08

Among these figures that for Gd is admittedly too low, and that for Sa is vitiated by the presence of europium in the material studied.

From the evidence presented in this Report, and in preceding years, we now feel justified in recommending the following changes in the table:—

Nitrogen,	from 14·04	to 14·01.
Bismuth,	„ 208·5	„ 208·0.
Tantalum,	„ 183·0	„ 181·0.
Terbium,	„ 160·0	„ 159·2.

Other changes which seem to be needed because of alterations in the atomic weights of silver and chlorine cannot yet be made with safety. The atomic weight of silver, as deduced from Stas's data, is probably too high, but by an unknown amount, and that will affect the entire table. If we assume, with Guye, that Ag = 107·89, with the proportional changes in Cl and Br, the atomic weight of barium, as determined by Richards, will be reduced by 0·05. Such a change, which is probably extreme, does not affect the utility of the accepted atomic weights at all seriously, and no important interest will suffer if we delay the suggested alterations until our knowledge of the corrections to be applied is more exact. Guye's conclusions, although strongly supported, are not final, and they should be neither accepted nor rejected except upon the basis of much more complete evidence than we now possess. The atomic weight of chlorine, as given in our last Report, is certainly too low, but it depends in part upon the undetermined change to be applied to silver. For that reason as well as for the reason that a change in chlorine affects many other values, we prefer to leave the figures as they are and to wait for fuller information. That information will doubtless be supplied by researches now known to be in progress, and the corrections which they will furnish ought not to be delayed very long.

One addition to the table seems to be legitimate. Europium, with an approximate atomic weight of 152, appears to be a definite element, as shown by the investigations of Demarçay, Urbain and Lacombe, Eberhard, and Feit and Przibylla. Its existence is recognised in Abegg's "Handbuch," and its claims to a place in the table are certainly as great as those of erbium, thulium, or terbium. As for dysprosium, its admission to the table may well be delayed until a better determination of its atomic weight shall have been made.

In conclusion, we urge upon all chemists who are engaged in the determination of atomic weights to send copies of their publications to all the members of this Committee in order that their work may be promptly recognised and not overlooked. Data published in standard journals are of course easily found, but publications of local societies and doctoral dissertations might readily escape our notice.

Professor Seubert, an original member of this Committee has resigned. Professor Ostwald has been designated as his successor. (See *Ber.*, 1906, xxxix., 2176 for the formal announcement of this change).

The Table offered for 1907 is appended hereto.

F. W. CLARKE,
HENRI MOISSAN,
WILHELM OSTWALD,
T. E. THORPE.

International Atomic Weights. (1907).

Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	75·0
Barium	Ba	137·4
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·96
Cadmium	Cd	112·4
Cæsium	Cs	132·9
Calcium	Ca	40·1
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·45
Chromium	Cr	52·1
Cobalt	Co	59·0
Columbium	Cb	94
Copper	Cu	63·6
Erbium	Er	166
Europium	Eu	152
Fluorine	F	19·0
Gadolinium	Gd	156
Gallium	Ga	70
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·0
Hydrogen	H	1·008
Indium	In	115
Iodine	I	126·97
Iridium	Ir	193·0
Iron	Fe	55·9
Krypton	Kr	81·8
Lanthanum	La	138·9
Lead	Pb	206·9
Lithium	Li	7·03
Magnesium	Mg	24·36
Manganese	Mn	55·0
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	143·6
Neon	Ne	20

Nickel	Ni	58·7
Nitrogen	N	14·01
Osmium	Os	191
Oxygen	O	16·00
Palladium	Pd	106·5
Phosphorus	P	31·0
Platinum	Pt	194·8
Potassium	K	39·15
Praseodymium	Pr	140·5
Radium	Rd	225
Rhodium	Rh	103·0
Rubidium	Rb	85·5
Ruthenium	Ru	101·7
Samarium	Sa	150·3
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·4
Silver	Ag	107·93
Sodium	Na	23·05
Strontium	Sr	87·6
Sulphur	S	32·06
Tantalum	Ta	181
Tellurium	Te	127·6
Terbium	Tb	159·2
Thallium	Tl	204·1
Thorium	Th	232·5
Thulium	Tm	171
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184
Uranium	U	238·5
Vanadium	V	51·2
Xenon	Xe	128
Ytterbium	Yb	173·0
Yttrium	Yt	89·0
Zinc	Zn	65·4
Zirconium	Zr	90·6

Of the following papers those marked * were read :—

*1. "*The Relation between Absorption Spectra and Optical Rotatory Power.* Part I. *The Effect of Unsaturation and Stereoisomerism.*" By Alfred Walter Stewart.

The author has examined the absorption spectra of certain saturated and unsaturated acids, and compared the results with the rotatory power of their amyl esters. The results show that a close relation exists between the general absorption power of compounds and their molecular rotation. The substance having the greater general absorption has also the greater molecular rotation. The case of the amyl esters of hydrocinnamic, cinnamic, and phenylpropiolic acids, which seems anomalous at first sight, agrees with this. An examination of the spectra of some stereoisomeric acids of the ethylene series showed that the rule holds in their case also. Experiments are in progress in other branches of the subject, for example, active and inactive isomerides, birotation, the influence of the solvent on the rotatory power, &c.

Discussion.

Dr. McKenzie pointed out that the values for the molecular rotations of the amyl esters of hydrocinnamic, cinnamic, and phenylpropiolic acid respectively, determined by Walden and quoted by the author, were obviously incorrect, since the amyl alcohol used by Walden in 1896 was a mixture.

Since it was now possible to separate the optically active constituent of fusel oil in a pure state by means of 3-nitrophthalic acid (*Ber.*, 1901, xxxiv., 485), he asked whether the author had prepared the pure esters in question and determined their rotations.

Mr. Stewart explained that owing to the complexity of the amyl spectrum it had been found best to examine the spectra of the acids and not those of the amyl esters. The cause of the change in rotation evidently is to be sought in the acidic part of the ester molecule. The results obtained by Sir W. H. Perkin in the case of the magnetic rotation of saturated and unsaturated acids agree with those observed in the case of optically active esters of the saturated and unsaturated series.

*2. "*Organic Derivatives of Silicon.* Part II. *The Synthesis of* dl-*Benzylethylpropylsilicol, its Sulphonation, and the Resolution of the Sulphonic Derivative into Optically Active Components.*" By Frederic Stanley Kipping.

dl-*Benzylethylpropylsilicol*, EtPrBzSi·OH, has been synthesised by the following series of reactions (compare *Proc.*, 1904, xx., 15) :—

$SiCl_4 + MgEtBr = SiEtCl_3 + MgClBr.$
$SiEtCl_3 + MgPhBr = SiEtPhCl_2 + MgClBr.$
$SiEtPhCl_2 + MgPrBr = SiEtPhPrCl + MgClBr.$
$SiEtPhPrCl + MgBzCl = SiEtPhPrBz + MgCl_2.$
$SiEtPhPrBz + H_2O (+ H_2SO_4) =$
$= SiEtPrBz{\cdot}OH + C_6H_6 (+ H_2SO_4)$

The silicol thus initially produced yields, with sulphuric acid, a mixture of sulphonic acids, of which one has been isolated in the form of its ammonium salt.

This acid is probably a derivative of the corresponding oxide, having the constitution—

$SO_3H{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiEtPr{\cdot}O{\cdot}PrEtSi{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H$;

it is the externally compensated compound, and although many of its salts with optically active bases crystallise unchanged, the *d*-methylhydrindamine salt can be resolved by crystallising fractionally from aqueous methyl alcohol.

The *dBdA*-salt is the more sparingly soluble and melts at about 205°; the impure *dBlA*-salt from the most soluble fractions melts at about 135°.

The *lBlA*-salt has been prepared by resolving the acid with *l*-methylhydrindamine.

The two optically active acids have very low specific rotations ($[\alpha]_D \pm 4°$ roughly), but there is ample evidence of their enantiomorphous relationship.

Discussion.

Dr. Lewkowitsch, referring to the statement that different melting-points were obtained with one and the same substance, asked whether this phenomenon was accompanied by the appearance of different colours, such as Jaeger had observed in the case of the liquid anisotropic phases of the esters of cholesterol and phytosterol at their different melting-points.

Prof. Kipping stated that the appearance of such colours had not been observed by him.

*3. "*The Association of Phenols in the Liquid Condition.*" By John Theodore Hewitt and Thomas Field Winmill.

The authors have determined the surface energy of several liquids, and find that the association of phenols is diminished or entirely inhibited by the presence of ortho-substituents. Comparison with meta- and para-isomerides has clearly shown that the effect is due more to the position than to the nature of the substituent group.

The effect of steric hindrance is also seen with the aromatic alcohols. Monophenylcarbinol (benzyl alcohol) is markedly associated at the ordinary temperature; the molecular weights of fused di- and tri-phenylcarbinol are, however, normal.

Discussion.

Dr. Hewitt, replying to the remarks of the President, said he supposed that probably they (the authors) had not encountered the best conditions for converting *o*-aminophenol into *o*-bromophenol. Respecting Mr. Baly's contention that any hindrance to association was structural rather than sterical, it was at least remarkable that the groups of larger molecular volume had a more marked effect than those, such as methyl and chlorine, whose molecular volume was smaller.

*4. "*A New Mercuric Oxychloride.*" By John Theodore Hewitt.

On allowing solutions of sodium hydroxide and mercuric chloride in sodium chloride to diffuse into one another, a layer of sodium chloride solution of intermediate density being interposed, very dark red crystals having the formula $Hg_6O_5Cl_2$ are deposited. These were at first considered to be red mercuric oxide or mercuric hydroxide, since on solution in hot dilute nitric acid and addition of silver nitrate solution no precipitate was obtained.

It has now been found that if a silver chloride precipitate is suspended in dilute nitric acid and mercuric oxide added, not only is the latter dissolved, but also the silver chloride.

In the estimation of chlorine in the oxychloride the latter was dissolved in warm dilute sulphuric acid, the mercury precipitated with sodium hyposulphite, and after oxidation of the excess of this reagent with dilute nitric acid, the chlorine was estimated in the usual way as silver chloride.

Discussion.

Dr. Hewitt was afraid he had not made the fact quite clear, that when silver chloride is dissolved in dilute nitric acid by addition of mercuric oxide the result is not to be attributed to the formation of a complex silver ion, but to the employment of the chlorine in forming complex ions with the mercury. The solubility of silver salts in albumenoid solutions mentioned by Dr. Divers was hardly of a similar nature, in the latter case solution depended rather on colloidal suspension.

*5. "*Preparation of Chromyl Dichloride.*" By Herbert Drake Law and Frederick Mollwo Perkin.

The authors find that the best method for preparing chromyl dichloride is to dissolve chromic acid in rather more than the equivalent quantity of concentrated aqueous hydrochloric acid, and to add to this solution concentrated sulphuric acid in small quantities at a time, the mixture being cooled between each addition. After standing for about twenty minutes in a tap funnel the heavy under layer of chromyl dichloride is drawn off. It can be purified by aspirating dry air through it and subsequent distillation. The yield is almost theoretical.

*6. "*Oxidation of Hydrocarbons of the Benzene Series.*" By Herbert Drake Law and Frederick Mollwo Perkin.

The authors have examined the products of oxidation of aromatic hydrocarbons by lead peroxide and manganese peroxide in acid solution, by chromyl dichloride, and by persulphates in acid solution in presence of silver salts.

The hydrocarbons investigated were toluene, the three xylenes, mesitylene, ψ-cumene, and cymene. In all cases varying yields of the monoaldehydes were obtained.

Toluene gave with lead peroxide 24 per cent of benzaldehyde, with manganese peroxide 5 per cent, with chromyl dichloride 44 per cent, and with persulphates 78 per cent. In the remaining cases, as a rule, the yield with chromyl dichloride was better than with the other oxidising agents, that obtained with persulphates being second. In general, lead peroxide gave a larger quantity of aldehyde than did manganese peroxide.

7. "*The Constitution of Silver Nitrate; a Correction.*" By Edward Divers.

In the opening paragraph of a paper which has just appeared (*Trans.*, 1906, lxxxix, 1900), Rây and Neogi state that the present writer is inclined to accept as fairly conclusive the evidence which they have adduced in favour of the oxylic constitution of silver nitrite.

In his note in the *Proceedings* (1905, xxi., 281), to which they make reference, no opinion at all is expressed as to the constitution of silver nitrite. The authors must have made the statement under some misapprehension of the writer's words, which he cannot account for.

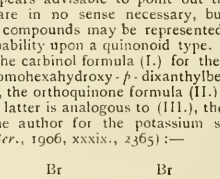
8. "*Aromatic Selenonium Bases.*" By Samuel Smiles and Thomas Percy Hilditch.

When anisole or phenetole are heated on the water-bath with selenium dioxide and aluminium chloride, the chlorides of the corresponding selenonium bases are formed. To isolate these substances, the reaction mixture is decomposed with water and freed from excess of phenolic ether by distillation in steam; finally the mixture is extracted with chloroform, which, on evaporation, leaves the chloride of the base as a red oil. *Trianisyl-* and *triphenetylselenonium chlorides* are viscous oils, the aqueous solutions of which yield strongly basic *hydroxides* on treatment with silver oxide. The *iodides* are sparingly soluble oils. The *platinichlorides* were obtained as brown precipitates, insoluble in water and very soluble in acetone. The *platinichloride* of *triphenetylselenonium* melts at 82—83°. The dichromates of these bases are insoluble in water, and are precipitated in yellowish-brown flakes when an acid solution of potassium chromate is added to solutions of the chlorides. They are very unstable, and turn dark on exposure to the air. *Trianisylselenonium dichromate* melts at 65—70°.

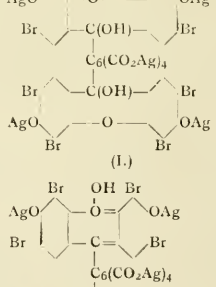
9. "*The Relation of Colour and Fluorescence to Constitution.*" By Arthur George Green.

In a paper bearing the above title (*Trans.*, 1906, lxxxvii., 1787), O. Silberrad has recently described a number of complex phthaleins formed by the condensation of mellitic and pyromellitic acids with resorcinol. From the fact that the silver salts of these phthaleins correspond to the substitution of hydrogen by silver, not only in all the carboxyl groups of the mellitic residue, but also in the two phenolic hydroxyl groups of each xanthene ring, it is concluded that "neither the colour nor the fluorescence of these compounds is dependent on the presence of quinone linkings, for in many cases a quinonoid structure is impossible." This conclusion Silberrad is inclined to extend to the phthaleins in general.

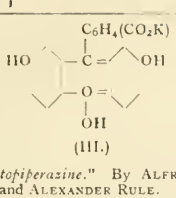
A study of the phthaleins of phenol and quinol, which the author has had in progress for some time past, has brought to light several facts pointing to an opposite conclusion, and strongly confirming the view that the coloured salts of these phthaleins have a quinonoid structure. It therefore appears advisable to point out that Silberrad's deductions are in no sense necessary, but that on the contrary his compounds may be represented with equal or greater probability upon a quinonoid type. For instance, in place of the carbinol formula (I.) for the silver salt of the octabromohexahydroxy-*p*-dixanthylbenzenetetracarboxylic acid, the orthoquinone formula (II.) may be substituted. The latter is analogous to (III.), the formula proposed by the author for the potassium salt of quinophthalein (*Ber.*, 1906, xxxix., 2365):—



(I.)



(II.)



(III.)

10. "*Tetraketopiperazine.*" By Alfred Theophilus de Mouilpied and Alexander Rule.

The authors have studied the action of sodium alkyloxides on esters of the type of ethyl oxamate, $NH_2{\cdot}CO{\cdot}CO_2Et$, whereby the elimination of 1 molecule of alcohol would be expected to give rise to ring compounds containing an imino-group. Ethyl oxamate should by such a reaction furnish oxalimide, $\begin{matrix} CO \\ | \\ CO \end{matrix}\!\!>\!NH$, which is referred to by Ost and Mente (*Ber.*, 1886, xix., 3228), but its existence appears to be very doubtful. The authors were not able to obtain it, but prepared from ethyl oxamate, *tetraketopiperazine*, which has twice the molecular weight of oxalimide, and which seems to be the substance described under the latter name.

Tetraketopiperazine was also obtained by the condensation of ethyl oxalate with oxamide; a *hydrazone*, *silver*, and *sodium* salts have been prepared, and the following constitutional formula is suggested:—

$$N\!<\!\begin{matrix} C(OH){\cdot}CO \\ CO \end{matrix}\!\!>\!\begin{matrix} CO \\ C \end{matrix}\!\!>\!NH.$$

Methyl succinamate yields succinimide by a similar reaction, and ethyl malonamate gives a *substance* of formula $C_6H_8O_3N_2$, resulting from the condensation of 2 molecules of malonamic acid through loss of 1 molecule of water.

A general method for the preferential saponification of a carboxyalkyl group occurring in the same compound with an acid amide group was described.

Saponified with alkali in the usual way, ethyl oxamate yields the semi-ethyl ester and oxalic acid, and ammonia is simultaneously evolved. By using the theoretical amount of pure sodium alkyloxide in dry benzene solution a large yield of sodium oxamate is obtained.

11. "*Transformations of Highly Substituted Nitroaminobenzenes. II. s-Tribromo-1-nitroaminobenzene.*" By Alice Emily Smith and Kennedy Joseph Previté Orton.

Treatment of 2 : 4 : 6-tribromo-1-nitroaminobenzene, $C_6H_2Br_3{\cdot}NH{\cdot}NO_2$, with sulphuric acid or a mixture of sulphuric and acetic acids leads to the replacement of a bromine atom by the nitro-group, and to the formation of 2 : 6-dibromo-4-nitroaniline (*Trans.*, 1902, lxxxi., 806). Within very narrow limits of temperature and concentration of the sulphuric acid, the nitroamine is partly converted into bromophenyliminobenzoquinones, analogous to the hexachlorophenyliminobenzoquinone obtained from *s*-trichloronitroaminobenzene (*Trans.*, 1905, lxxxvii., 389). In the case of the bromo-compounds, however, a mixture of two phenyliminobenzoquinones is always formed, namely, a penta- and a hexa-bromo-derivative, $C_6H_2Br_3{\cdot}N : C_6H_2Br_2 : O$ and $C_6H_2Br_3{\cdot}N : C_6HBr_3 : O$; bromine is accordingly set free in the reaction.

s-Tribromophenyliminodibromobenzoquinone crystallises in dark red prisms or needles with a metallic lustre, and melts at 171°. On reduction it yields *s-tribromophenyldibromo-4-hydroxyphenylamine*, which crystallises in white, silky needles melting at 155—156°, and is freely soluble in alcohol and other solvents. The latter can thus be separated from the *s-tribromophenyltribromo-4-hydroxyphenylamine*, which crystallises in colourless needles or prisms melting at 206°. On oxidation it is converted into *s-tribromophenyliminotribromobenzoquinone*, which crystallises in pale red needles or prisms melting at 134—135°, and is more soluble than the pentabromo-derivative in all the usual solvents.

12. "*Resolution of Tetrahydro-p-toluquinaldine into its Optically Active Components.*" By Thomas Constantine Beck and William Jackson Pope.

The *d*-α-bromocamphorsulphonic acid of Armstrong and Lowry was shown to be applicable for the resolution of externally compensated bases, in accordance with the method of Pope and Peachey, by using it for the separation of the optically active tetrahydro-*p*-toluquinaldines from the corresponding externally compensated mixture. By treating two equivalents of *dl*-tetrahydro-*p*-toluquinaldine hydrochloride with one equivalent of the ammonium salt of the Armstrong and Lowry acid, under appropriate conditions, a nearly quantitative separation of *d*-tetrahydro-*p*-toluquinaldine-*d*-α3-bromocamphorsulphonate is obtained; the salt gives the value $[M]_D + 445$ in aqueous solution. On treating the base retained by the mother liquors with Kipping and Pope's *d*-bromocamphorsulphonic acid, nearly the whole of the *l*-base can be separated in a pure state as described by Pope and Rich.

The molecular rotatory powers of a number of salts of the optically active bases have been examined and found to be in agreement with previous conclusions concerning these values for salts of strong optically active bases with strong acids.

13. "*Note on the Theory of Valency.*" By William Barlow and William Jackson Pope.

The homogeneous, close-packed assemblages of spheres corresponding to a series of homologous compounds, such as, for instance, the normal paraffins, are characterised by similarity of marshalling. Further, the assemblage representing ethane is derived from that of methane (*Trans.*, 1906, lxxxix., 1743) by an application of the second geometrical property (*loc. cit.*, 1729); the substitution of one carbon sphere of volume 4 for a hydrogen sphere of volume 1 in each unit, CH_4, of the partitioning of the methane assemblage necessitates the simultaneous addition of three hydrogen spheres in accordance with the second geometrical property, so that each unit of the ethane partitioning assumes the composition C_2H_6.

The empirical compositions, CH_3 and CH_4, of the ethane and methane assemblages differ, however, by one hydrogen sphere, and a case is thus provided in which, so far as the packing of the spheres is concerned, two hydrogen spheres of volume 1 in the methane assemblage perform the functions of one hydrogen sphere of volume 1 in the ethane assemblage. This is therefore a case of the kind which Mr. D. L. Chapman (*Proc.*, 1906, xxii., 320) considers to offer difficulty in connection with our theory of valency, and to necessitate some modification of the fundamental assumptions. From the fact that the methane and ethane assemblages are related through the second geometrical property, it is, however, clear that the application of Mr. Chapman's argument to an actual instance merely brings out the very close correspondence between the geometrical properties in question and our knowledge of chemical constitution.

Just as the bearings of the doctrine of valency on constitution and substitution do not appear when empirical compositions are considered, so the second geometrical property only serves to elucidate the doctrine of valency when it is applied in connection with the molecular composition, or the composition of the unit of the geometrical partitioning of the assemblage. A number of examples of the mode in which the property is applied have been already given (*loc. cit.*, 1729—1736).

We may perhaps be allowed to take this opportunity of emphasising the statement (*loc. cit.*, 1691 and 1698) that the geometrical properties and the assemblages, which latter are for diagrammatic purposes represented as if composed of undeformed spheres, are in every case supposed to be subject to the condition that so much general pressure is operative on the system as practically to eliminate the interstitial space. It is, of course, not conceivable that the space occupied by the spheres of influence of a group of atoms in contact should include space unavailable for occupation by the atoms.

(To be continued).

NOTICES OF BOOKS.

The Principles of Qualitative Analysis. By WILHELM BÖTTGER. Translated by WILLIAM GABB SMEATON. London: Rebman, Ltd. 1906.

UNDER favourable conditions the teaching of qualitative analysis may become a valuable training and mental discipline, and Prof. Böttger's book is well adapted to aid the teacher to expound the subject in a thoroughly scientific manner and in accordance with modern conceptions. Much attention is paid to the electrolytic theory and the law of mass action, the fundamental law governing chemical equilibria. The plan adopted in the earlier part of the book, which treats of testing a solution for metals, is to explain, first of all, the method of identification of one metal, and then give directions for the preparation of a solution of a salt of it, with which the reactions and properties of the metallic ion may be studied. This appears a very satisfactory procedure, and should give the student help in acquiring a good grasp of the general tests for each group and the distinguishing reactions of each metal of the groups. The anions are then similarly dealt with, a more systematic classification being adopted than is generally put before the student. The method of attacking the complete analysis of one unknown is also discussed, and general analysis tables are given. The book appears to be more adapted to the requirements of teachers than of students, or at any rate to be used by the latter not in the laboratory, but as a supplement to a simpler text-book of qualitative analysis; there can be, however, no question that it is a particularly valuable treatise on the general principles and methods.

A Laboratory Course of Organic Chemistry. By ARTHUR W. TITHERLEY, D.Sc. (Vict.), D.Sc. (Liv.), Ph.D. (Heidelb.). London: George Philip and Son, Ltd. Liverpool: Philip, Son, and Nephew, Ltd. 1906.

THIS book contains directions for general practical work in organic chemistry, including both preparations and the isolation and identification of the more common organic compounds. The course is graduated in difficulty, and begins with the description of simple manipulations and processes, with which, we may remark in passing, the student's inorganic work would probably have made him familiar. Fractional distillation is well explained, and full directions are given for the preparation of many important or typical substances, a good feature being the mention of the yield which should be obtained if the processes are carried out according to the detailed explanations. The experiments on the identification of the more representative classes of compounds are very systematically arranged, and the book should be a useful supplement to lecture-work on elementary organic chemistry. The alkaloids are especially well treated, and the author shows himself to be fully qualified to assist in bringing into instruction in organic chemistry some of that system which at present it generally lacks, and the want of which makes it compare unfavourably with inorganic chemistry as an educational training in the eyes of many teachers.

John Dalton. By J. P. MILLINGTON, M.A., B.Sc. London J. M. Dent and Co. New York: E. P. Dutton and Co. 1906.

THE account of the struggles of John Dalton against adverse circumstances in his early years is to modern chemists encouraging reading, when they reflect on the outcome of his patience and perseverance, and the student of science does not live who could find these biographical sketches of English men of science dull or uninspiring. The steps by which Dalton arrived at his great generalisation are traced with marked lucidity in this volume, and the elaboration of his views regarding the atomic structure of matter is critically surveyed, while his marvellous power of marshalling his facts and making deductions from them is clearly set forth. His experimental work is perhaps somewhat undervalued, for he undoubtedly acquired a considerable amount of dexterity, especially in the handling of gases, though it cannot be disputed that it was as a thinker that he made his greatest mark; nevertheless, if it had not been for his remarkable achievements in this direction in all probability his experimental work would have been more appreciated, and he certainly possessed a unique talent for the collection of material upon which to base his theories. The present time, when speculations as to the nature of matter are rising on every side, is well fitted for the publication of this excellent little biography of our great chemist, who was so well equipped from a physical point of view to lay the foundations of modern physical chemistry.

Die Fabrikation des Russes und der Schwärze. ("The Manufacture of Soot and Carbon Blacks"). By Dr. HIPPOLYT KÖHLER. Second Edition. Braunschweig: Friedrich Vieweg und Sohn. 1906.

THE author of this small book has had much experience in the manufacture of carbon blacks, and his opinion, especially upon practical points, is of great value. The subject is treated more particularly from the point of view of the utilisation of by and waste products, and the production of decolorising charcoal is considered at length. In the second edition the first part is practically unchanged, although a chapter has been added on advances in the making of soot during the last twenty years. The second part of the book, on the other hand, has necessarily been much extended owing to the variety of new processes which have come into use in the manufacture of carbon blacks. A section on the examination and valuation of soot and carbon blacks describes all the usual methods, and an attempt is made to give practical methods for the identification and separation of the different products. Colour tests and the measurement of colouring power are treated only briefly, and the second on methods of examination might perhaps have been somewhat enlarged with advantage.

Untersuchungen uber Künstliche Parthenogenese. ("Researches on Artificial Parthenogensis"). By JACQUES LOEB. German Edition by E. SCHWALBE. Leipzig: Johann Ambrosius Barth. 1906.

THE German translation of Prof. Loeb's work on Parthenogenesis has been prepared with the sanction and help of the author, who has contributed to it a preface, in which he briefly describes the aim and scope of the book. In order to get an insight into the essential nature of fertilisation he believes that the chemical and physical agents which influence it must first be sought, and that then their action must be further and more accurately investigated. The author's experiments are not yet by any means concluded, but the account of them, so far as they go, makes a book which all biologists will be glad to read, even if many of them dissent from the conclusions drawn in it. The translation has been carefully performed, and the sense of the original has been faithful reproduced.

Gmelin-Kraut's Handbuch der Anorganischen Chemie. ("Gmelin and Kraut's Handbook of Inorganic Chemistry"). Edited by A. HILGER and C. FRIEDHEIM. Seventh Edition. Heidelberg: Carl Winter. 1905.

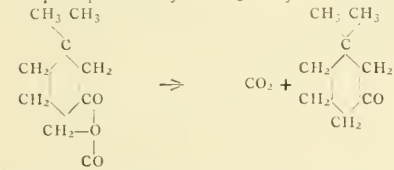
THE seventh edition of Gmelin and Kraut's text-book of inorganic chemistry, which is now in course of publication, is one of the most comprehensive and thorough works on the subject which has ever been produced, and possesses many distinctive characteristics, which will recommend it as a reference book and dictionary of chemistry. Hardly any other work can approach it in completeness and in the abundance of references to original papers, and the arrangement of the great mass of material which the authors have accumulated is most convenient. The text-book is to appear in 70 parts, and the editors hope that the publication of the seventh edition will be completed in the course of the years 1908 or 1909.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

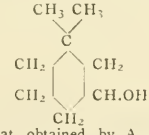
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 3, January 21, 1907.

Conditions of Stability of the Carbylamines.—H. Guillemard.—This author has previously indicated methods that may be employed for the estimation of mixtures of nitriles and carbylamines. On applying these methods to the investigation of the alcoholisation of metallic cyanides, he finds that, if, in numerous instances, carbylamines are not obtained, the fact is to be explained by the conditions of the experiment either giving rise to isomerism with their transformation into nitriles, or causing their combination with some body present to form compounds incapable of generating them, or causing decomposition. From the facts collected experimentally, the conclusion is, on the one hand, that the carbylamines tending to form themselves may disappear by combining readily with the agents of alcoholisation, which give rise to them, if they are not isolated in the state of stable combination with the cyanide; on the other hand, that they readily form isomers under the influence of heat, after having given rise to an intermediate compound, which might be a combination with a cyanide or a polymer able itself to change to a nitrile. It is thus manifest that a carbylamine is not obtained by alcoholising a cyanide, if the latter is able to form a stable combination with the nascent carbylamine.

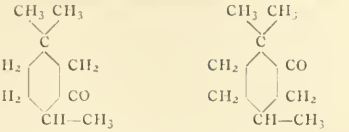
Synthesis of Derivatives of Cyclohexane : 3.3-Dimethyl and 3.3.6-Trimethylcyclohexanones.—G. Blanc.—The author has previously demonstrated that *ββ*-dimethyl and *ββε*-trimethylpimelic acids may be obtained synthetically by a series of reactions. These two acids readily close their chain with loss of CO_2, furnishing the corresponding hexanones, the process being the well-known classical method of calcination of the calcium salt. The author found it most practical to transform the acid into the anhydride by means of acetic anhydride, distilling the latter slowly at the ordinary pressure. The reaction then takes place quantitatively into CO_2 and cyclohexanone.



ββ- (or 3.3) dimethylcyclohexanone, already described by Léser, who obtained it by treating acetylcyclomethylheptenone with aqueous potash, is a colourless mobile liquid with an odour of menthone; it boils at 173°. Its semicarbazone crystallises in dilute alcohol in needles fusing at 203° over mercury. Reduced by sodium and absolute alcohol it is converted into an alcohol—



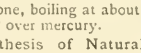
identical with that obtained by A. W. Crossley and N. Renouf, starting from 1.1-dimethyldihydroresorcin. This alcohol is an oily liquid with a camphor-like odour, boiling at 78° (15 mm.), solidifying in ice, and then melting towards 12°. The slow distillation of *ββε*-trimethyl pimelic anhydride leads similarly to *ββε*- (or 3.3.6) trimethylcyclohexanone, the constitution of which is similar to that of the pulenone of Wallach and Kempe:—



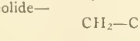
3.3.6-Trimethyl-cyclohexanone. Pulenone.

This new ketone is a mobile liquid with a strong odour of menthone, boiling at about 186°; its semicarbazone melts at 170° over mercury.

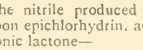
Synthesis of Natural Erythrite.—R. Lespieau.—The author has previously notified the formation of buteneolide—



from the nitrile produced by the action of hydrocyanic acid upon epichlorhydrin, and the further production of an erythronic lactone—



The compound thus obtained has no action upon polarised light, but the presence within the molecule of two asymmetric carbon atoms, not mutually neutralising each other, led to the supposition that the inactivity was due to the presence of optical inverses in equimolecular proportions. On the other hand, if stereochemically four bodies can be represented corresponding to the formula,—



it is obvious that only two of them could arise from the fixation of two hydroxyls upon butene-2-olide, those two being those in which the hydroxyls are on the same side of the plane of the ring corresponding to this closed chain. Thus hydrolysis of the inactive lactone would give inactive erythrite on this supposition. The author has verified these consequences of stereochemistry by changing the inactive lactone (1) to a levorotatory lactone, (2) to natural erythrite. The synthesis completely agrees with the stereochemical views. The lactone, which formed the starting point, belonged to the maleic series.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th instant, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Sir David Gill, K.C.B., Mr. S. A. Ionides, The Hon. George Peel, and Mr. H. M. Phipson were elected Members. The Special Thanks of the Members were returned to Dr. Ludwig Mond, F.R.S., for his Donation of £300, and to Professor Sir James Dewar, F.R.S., for his Donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures.

The Rothamsted Experimental Station (Lawes Agricultural Trust) has received a donation of £2000 from the Permanent Nitrate Committee, to be invested and added to the general endowment fund of the Station. A donation of one hundred guineas has also been received from the Fertiliser Manufacturers' Association. During the past summer the Station entered into occupation of the "James Mason" Bacteriological Laboratory, the gift of Mr. J. F. Mason, M.P. The Society for extending the Rothamsted Experiments, which was formed to obtain funds wherewith the Experimental Station might enlarge the scope of its work and initiate further agricultural in-

vestigations, has further received, during the past year, subscriptions and donations amounting to £240. Further subscriptions are still urgently needed to secure a more adequate staff, and may be addressed to the Secretary of the Rothamsted Experimental Station, Harpenden, Hertfordshire.

Manufacture of Paints and Colours.—The Chief Inspector of Factories forwards a copy of the Regulations made by the Secretary of State for the Manufacture of Paints and Colours. They will apply, except where otherwise indicated in the Regulations, to all factories and workshops engaged in that manufacture in which dry carbonate of lead or red lead is used, or chromate of lead is produced by boiling. The Regulations came into force on the 1st February, 1907, and supersede the Special Rules for the manufacture of paints and colours established under the Factory and Workshop Act, 1891. A copy of the Regulations must be kept affixed in a conspicuous place in every factory and workshop to which they apply. Under Regulations 4 and 11 every person employed in a "lead process," or at the roller mills connected with the grinding in oil of "lead colour," must be medically examined once in each calendar month *at the appointed time* by the Certifying Surgeon of the district, unless some other medical practitioner is specially appointed for the purpose by the Chief Inspector of Factories. The time appointed for examination must be made known to all workers concerned, and arrangements should be made for due privacy. The Surgeon will be required to forward annually to the Home Office a return of the examinations and suspensions during the year.

Some Sulphates of Tetravalent Vanadium.—Gustave Gain.—MM. Koppel and Behrendt have obtained a certain number of vanadyl sulphates by dissolving V_2O_5 in concentrated sulphuric acid and reducing the solutions with SO_2. Other sulphates belonging to the same group have been prepared by the author according to a different method, which starts from the azure-blue solution, obtained by treating the mixture of V_2O_3 and V_2O_4 with a saturated solution of SO_2. By different treatments, the following sulphates were isolated and analysed :—

$2V_2O_4.5SO_3.18H_2O$	Azure-blue crystals
$2V_2O_4.6SO_3.20H_2O$	Turquoise-blue crystals
$2V_2O_4.7SO_3.20H_2O$	Blue-green crystals
$2V_2O_4.9SO_3.22H_2O$	Clear blue crystals
$2V_2O_4.10SO_3.24H_2O$	Very clear blue crystals

These may be written in the following series :—

$$2SO_4(VO)+3H_2SO_4+16H_2O,$$
$$2SO_4(VO)+4H_2SO_4+16H_2O,$$
$$2SO_4(VO)+5H_2SO_4+15H_2O,$$
$$2SO_4(VO)+7H_2SO_4+15H_2O,$$
$$2SO_4(VO)+8H_2SO_4+16H_2O.$$

—*Comptes Rendus*, cxliii., No. 26.

Method of Determining Transition-points.—K. Beck and K. Ebbinghaus.—If a substance which can exist in different modifications in the solid state is fused in a test-tube, and the melt is put after solidification into a cooling bath (a beaker full of water), as the temperature gradually sinks a visible change occurs in the structure of the melt. At a temperature a little below the melting point the walls of the test-tube appear to be completely covered with a deposit of crystals, but as the temperature falls this deposit detaches itself from the glass walls, often with a crackling noise. It was found that there is a definite temperature above which the deposit is visible and below which the substance separates off from the walls. From a great number of experiments it was concluded that this peculiarity of change of structure is widely distributed, so that a method of characterising and identifying substances can be based upon it. The authors experimented with sulphur, ice, benzophenone, *p*-dibrombenzene, *p*-dichlorbenzene, &c. ; also with mixtures of the last two named compounds. The experiments with sulphur were performed in order to test the method with reference to the transition S rhombic $\rightleftharpoons$ S monoclinic. The transition-point is 95·5°, *i.e.*, below this temperature the rhombic form is stable and above it the monoclinic modification is stable. With rhombic sulphur it was found that from 25° to 90° the glass walls were quite clear, at 95° traces of a deposit were seen, at 96° it was more distinct and rapidly increased, and at 115° the specimen had not melted, but it melted at 120° to 121°. The heating was arranged so that the increase of temperature was 1° in every forty-five seconds. These experiments were repeated many times, and it was found that the method affords a convenient means of determining the transition-point.—*Berichte*, xxxix., No. 15.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Society of Arts, 8. (Cantor Lectures) "Gold Mining and Gold Production," by Prof. J. W. Gregory.

TUESDAY, 12th.—Royal Institution, 3. "The Visual Apparatus of Man and Animals," by Prof. William Stirling.

WEDNESDAY, 13th.—Society of Arts, 8. "Motor Omnibuses," by Lord Montagu of Beaulieu.

THURSDAY, 14th.—Royal Institution, 3. "The Minute Structure of Igneous Rocks and their Significance," by Mr. A. Harker.

—— Society of Arts, 4.30. "The Practical Side of Famine in India," by Sir Frederic S. P. Lely.

FRIDAY, 15th.—Royal Institution, 9. "Foraminifera," by Mr. J. J. Lister.

SATURDAY, 16th.—Royal Institution, 3. "Röntgen, Cathode, and Positive Rays," by Prof. J. J. Thomson.

BIRKBECK COLLEGE,
Breams Buildings, Chancery Lane, E.C.

SCIENCE CLASSES, DAY & EVENING—

CHEMISTRY .. .. .. ALEX. MCKENZIE, Ph.D., D.Sc, M A.
PHYSICS .. .. A. GRIFFITHS, D.Sc.
MATHEMATICS .. .. E. H. SMART, M A.
BOTANY .. .. V. H. BLACKMAN, M.A.
ZOOLOGY .. .. H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY J. W. EVANS, D.Sc.
METALLURGY, MINING, and ASSAYING .. .. G. PATCHIN, A.R.S.M.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2461.

BORIC ACID: ITS DETECTION AND DETERMINATION IN LARGE OR SMALL AMOUNTS.*

By WILSON H. LOW.

(Concluded from p. 62).

Quantitative Test (continued).

The following results are from an actual test:—Fifty grms. of meat taken + 25 cc. N/2 sodium carbonate solution.

First distillate, about 100 cc. After making alkaline to nitrophenol, took about 5·90 cc. N/1 sodium hydroxide to phenolphthalein end-point. Enough to make in all 17·7 cc. of the N/1 sodium hydroxide were added. After evaporating off the alcohol and getting the residue in proper solution, the titration for boric acid took 4 cc. of N/1 sodium hydroxide + 21·7 cc. N/10 sodium hydroxide, equivalent to 61·70 cc. N/10 solution in all. Deduct 0·25 cc. for the glycerol blank leaves 61·45 cc. as due to the boric acid in the first 100 cc. of distillate.

The boiling and distillation flasks are set on asbestos cloth and held in retort rings and clamps.

The apparatus works perfectly and I cannot say too much about the absolute necessity of the boiling tube at every stage where methyl alcohol is boiled in glass. In a metal dish it will boil without bumping, but not in glass. The boiling flask has some phenolphthalein added to it and enough concentrated sodium hydroxide (practically carbonate-free) to keep it permanently red. This insures no boric acid in the vapour.

All stoppers are of cork.

Second distillate, about 100 cc., took 6 cc. N/10 sodium hydroxide, for the boric acid. This minus 0·25 for the glycerol blank leaves 5·75 cc. for the boric acid. The preliminary titration in methyl alcohol solution had indicated about 5·50 cc.

Third distillate, about 100 cc., took 0·57 cc. N/10 sodium hydroxide, and this minus 0·25 cc. for the glycerol blank leaves 0·32 cc. for the boric acid.

Fourth distillate, about 50 cc., took 0·25 cc. N/10 sodium hydroxide, and this is the quantity taken by the glycerol alone, so all the boric acid has been obtained.

Total N/10 sodium hydroxide used for boric acid = 67·52 cc. and this multiplied by 0·0062 = 0·4168 grm. = 0·837 per cent. on the meat taken.

This is a large quantity to be present under the circumstances and was more than I expected. Had it not been for the preliminary titration in methyl alcohol solution, enough alkali to retain the boric acid might not have been added and loss would have occurred while evaporating off the methyl alcohol. Had more calcium chloride been added at the start the first two distillates would probably have contained all the boric acid.

Action of Boric Acid on some Indicators.—In all the following experiments, unless otherwise stated, the water used was free from carbon dioxide.

A solution of more than 2 grms. of boric acid in 100 cc. will react acid to methyl orange and also to nitrophenol, more so to the latter than the former. Direct experiments have shown, however, that nitrophenol gives perfectly accurate results in boric acid titration, if carried out as directed. It is a great advantage to expel all carbon dioxide, and this applies to methyl orange as well.

Loss of Boric Acid on Ignition with Organic Matter.—On igniting boric acid and meat, strongly, to burn off as much carbon as possible, greenish flames were seen, and the ash when tested gave a very slight qualitative test for boric acid, while there had been enough originally present to give a strong test.

Numerous experiments have been made to test the process at every essential point. Instead of giving the experiments in detail it will, perhaps, be sufficient to give in direct statements the results.

1. A solution containing a small amount of boric acid may be concentrated from 100 cc. to 10 cc. without fear of a titratable amount of boric acid being lost.

2. Boiling a dilute solution of boric acid to free it from carbon dioxide occasions no loss, unless the boiling is prolonged.

3. All carbon dioxide is expelled from distilled water by heating to boiling and then applying vacuum for a few minutes till the solution is almost cold.

4. Starting with a mixture in the distillation flask of 25 cc. of water and 25 cc. of methyl alcohol and passing methyl alcohol vapour through the mixture, while keeping the latter approximately at the same volume, it took fifty-five minutes and over 400 cc. of distillate before the temperature of the vapour leaving the distillation flask was anywhere near the boiling-point of methyl alcohol, showing the difficulty of driving off the water.

5. Ten cc. of boric acid solution containing 0·3125 grm. and 40 cc. methyl alcohol were distilled with methyl alcohol vapour. Seven successive distillates failed to get over all the boric acid.

6. Where a water trap was not used the boric acid recovered was, in a certain case, equivalent to 4·90 cc. N/1 sodium hydroxide. Where a water trap was used 5·05 cc. N/1 sodium hydroxide were required. Theory called for 5·04 cc.

7. By distilling a mixture of one volume of aqueous solution of boric acid with ten volumes of methyl alcohol, till only 3 cc. of the mixture were left, about four-fifths of the boric acid were found in the distillate and one-fifth left in the flask.

8. It was found that if calcium chloride was added to the distillation flask in the proportion of about 0·5 grm. for each cubic centimetre of solution, all the boric acid came over quickly and completely. Using two-thirds of a grm. of calcium chloride is better yet, unless some conditions make it impracticable to use this amount.

Notes.

Make sure the methyl alcohol and calcium chloride used give no distillate containing a titratable quantity of boric acid. This may be insured by placing the calcium chloride in a separate flask, connecting with the distillation apparatus, acidifying with several drops of hydrochloric acid, and passing methyl alcohol vapour through till the distillate gives no titration for boric acid. This solution of calcium chloride is then added to the test instead of the solid salt. Nickel dishes or deep crucibles are very good for evaporating off alkaline solutions of methyl alcohol containing boric acid. No boiling tube is required. While our method of freeing the solution from carbon dioxide, by boiling under a vacuum after heating on the steam-bath, appears all that could be desired, it is not suitable for freeing a solution of calcium bicarbonate from excess of carbon dioxide. Actual boiling under atmospheric pressure is required in this case as direct experiments have shown.

Sometimes iron appears to distil over with the methyl alcohol, when the contents of the distillation flask are strongly acid. This causes the end-point with nitrophenol to be somewhat obscure, as the solution will take on a reddish tinge before the strong yellow due to excess of alkali. It makes the solution look as if the phenolphthalein end-point was about to be reached, before the nitrophenol end-point had been seen. This has only occurred a few times and did little harm. This was noticed so recently, that I have not proved it to be caused by iron, but it appears to be iron,

* From the *Journal of the American Chemical Society*, xxviii., No. 7.

In conclusion, I would like to draw attention to the very wide distribution of boric acid. It occurs in almost everything we meet in the food line, and caution should be used in reporting food as containing boric acid as a preservative without a quantitative determination. Ten grms. of food product are quickly burned to ash and 50 to 100 cc. of methyl alcohol distilled from this ash will contain most of the boric acid, or even all, unless it is present in some quantity. Now one drop of N/10 sodium hydroxide on this quantity will equal 0·0031 per cent. of boric acid, much too small a quantity to have been added for preserving purposes, and yet large enough to have given a strong qualitative test.

Boric acid occurs naturally in apples and probably in other fruits and vegetables. It is present in almost all common salt and some kinds contain relatively considerable amounts of it.

Below will be given some results on salts used in packing-house products. The results are rather under than over the truth, as some of the tests were made without all the necessary refinements of the process as it now stands.

Designation of the salt.	Boric acid. Per cent.	Grains per pound avoir.
Kansas No. 2 rock salt ..	0·005000	0·35
Foreign sea salt	0·010900	0·76
Foreign sea salt	0·006448	0·45
Cheshire salt	0·000992	0·07
XXX Casing salt	0·000620	0·0435
Kansas fine salt	0·000620	0·0435
Kansas rock salt, No. 2 ..	0·001240	0·0870
Louisiana rock salt	0·000992	0·06944

There is not a salt here but what would give a good qualitative test by the delicate method indicated in this paper, and some of them would show up under the less refined test of the steam-bath.

PRESENTATION TO PROFESSOR RIGHI.

A CIRCULAR, of which the following is the English version, has been sent in English, Italian, French, and German, by an influential Committee, to all men of science likely to be interested in the work which Professor Righi has so successfully carried on for twenty-five years.

SIR,—It is both right and just that those men of highest merit, who by their genius and doctrine have added to the patrimony of science and have opened up new ways to the progress of humanity, should feel and see how much esteem and affection has sprung up and grown around them, slowly and yet vigorously, perhaps without their having perceived how much they are esteemed and loved.

A few friends and admirers wish that this should be so in regard to Senator Professor Augusto Righi. They have therefore thought of celebrating by a ceremony which is to be kept strictly intimate, as such is more counted to please the illustrious professor, the 25th anniversary of his university teaching, together with the occasion of the transferment to a worthier site of the Physical Institute, over which he presides and renders each day more glorious.

This ceremony will take place the day on which he will deliver his first lecture at the new Institute, and will consist in the presentation of a bronze bust, to perpetuate throughout future generations the likeness, and through their means the gifts of vigor in intellect and soul that the beloved Master reveals in his features.

We beg to announce that the ceremony will take place February 20th in the certainty that the adhesion of one so well-known in science as yourself would be most welcome to Professor Righi.

THE COMMITTEE.

Bologna, R. Universitá.
January 20th, 1907.

THE CARRYING DOWN OF AMMONIUM OXALATE BY OXALATES OF THE RARE EARTHS.*

By GREGORY PAUL BAXTER and ROGER CASTLE GRIFFIN.

(Concluded from p. 64).

NEODYMIUM oxalate, which had been precipitated by addition to a nearly saturated solution of ammonium oxalate, was found to contain a still larger proportion of ammonium oxalate.

	I.	II.	III.	Average.
Per cent of Nd_2O_3	49·56	49·70	49·59	49·62
Per cent of C_2O_3	39·63	39·66	39·66	39·65
Per cent of $H_2O + NH_3$ ..	9·91	10·31		10·11
Total..				99·38

$$\text{Ratio, } M_2O_3 : 3C_2O_3 = \frac{49·62}{39·65} = 1·2514$$

$$M = 111·2 \quad (Nd = 143·6)$$

Upon the assumption that the average atomic weight of the metals in this sample is 144·2, the amount of C_2O_3 corresponding to 49·62 per cent of oxide is 31·86. The difference between this proportion and that observed is 7·79, which in turn corresponds to 3·68 per cent of ammonia. In order to determine whether this proportion of ammonia actually existed in the oxalate, the latter was analysed for ammonia. Weighed portions of the oxalate were dissolved in dilute sulphuric acid, and the solutions were diluted to about one-half litre. Then they were transferred to a litre retort, into the tubulature of which was fitted a dropping funnel containing a strong solution of ammonia-free potassium hydroxide. The potassium hydroxide was slowly added to the solution in the retort, and the ammonia set free was distilled into standard hydrochloric acid in the usual way. Blank tests were made, and slight corrections were applied. The percentage of ammonia obtained experimentally agrees very closely with that calculated above.

	I.	II.	III.	IV.	Average.
Weight of oxalate..	0·4343	0·2872	0·3290	0·3098	
Cc. N/10 HCl used .	9·22	6·10	6·76	6·46	
Per cent of ammonia	3·61	3·62	3·55	3·55	3·58
Calculated..					3·68

Next, precipitation in neutral solution with ammonium oxalate was investigated. A solution of neodymium chloride as nearly neutral as possible was prepared by evaporating to dryness on the steam-bath a solution of the oxide in hydrochloric acid, and repeating the evaporation several times after dissolving the residue in water. This solution was added drop by drop with continual agitation to a concentrated hot solution of ammonium oxalate. Occlusion is to be expected to the same extent here as in the previous case. Such proved to be the result.

	I.	II.	III.	Average.
Per cent of Nd_2O_3	49·57	49·49		49·53
Per cent of C_2O_3	39·25	39·24	39·25	39·25
Per cent of $H_2O + NH_3$ ..	11·28	11·74		11·51
Total..				100·29
Per cent of NH_3	3·50	3·50		3·50
Per cent of C_2O_3 corresponding to NH_3				37·41
Per cent of C_2O_3 corresponding to Nd_2O_3 ..				31·84

$$\text{Ratio, } M_2O_3 : 3C_2O_3 = \frac{49·53}{31·84} = 1·5555$$

$$M = 144·0 \quad \text{Theoretical} = 144·2$$

It has been pointed out by Richards that occlusion of any substance is proportional to the concentration of that

* From the *Journal of the American Chemical Society*, xxviii., No. 12.

substance in the molecular condition at the moment of precipitation (*Proc. Am. Acad.*, xxxv., 377; xxxvi., 377). In the present instance, since ammonium oxalate is the substance occluded, occlusion should increase with increasing concentration of molecular ammonium oxalate at the moment of precipitation. This has already been found to be the case when precipitation is carried out in neutral or very nearly neutral solution. In a solution containing much strong acid, however, the concentration of molecular ammonium oxalate would be very low, for the reaction between the hydrogen ion and the oxalate ion is nearly complete, even when the hydrogen ion concentration is not large. In the case of nitric acid the equilibrium with ammonium oxalate may be represented as follows:—

$$\begin{array}{ccccc} 2NH_4^+ & + & C_2O_4^{--} & \rightleftarrows & (NH_4)_2C_2O_4 \\ + & & + & & \\ 2NO_3^- & + & 2H^+ & \rightleftarrows & HNO_3 \\ \uparrow\downarrow & & \uparrow\downarrow & & \\ 2NH_4NO_3 & & H_2C_2O_4. & & \end{array}$$

If then neodymium oxalate is precipitated by ammonium oxalate in the presence of much nitric acid, little or no carrying down of ammonium oxalate is to be expected.

In the next experiment neodymium nitrate was added to a hot nearly saturated solution of ammonium oxalate containing a large amount of nitric acid. The precipitate was washed with hot water, dried, powdered, and analysed as before. The analysis of the precipitate confirms the prediction made above. The precipitate contained a mere trace of ammonia, which may account for the slight difference between the observed and theoretical results.

	I.	II.	Average.
Per cent of Nd_2O_3 ..	52·73	52·73	52·73
Per cent of C_2O_3 ..	33·90	33·91	33·91
Per cent of H_2O ..	12·39	12·53	12·46
Total..			99·10

$$\text{Ratio, } M_2O_3 : 3C_2O_3 = \frac{52·73}{33·91} = 1·5551$$

$$M = 144·0 \quad \text{Theoretical} = 144·2$$

Praseodymium oxalate also was studied in the same way. To a solution of praseodymium nitrate containing nitric acid, an excess of oxalic acid solution was added, drop by drop, with continual agitation. The oxalate, was thoroughly washed with water, dried in an air bath, powdered in a mortar, and analysed as in the case of neodymium. The oxalate, upon ignition, was eventually converted into a black oxide, of the composition Pr_4O_7 (Dammer, *Handb. der Anorg. Chem.*, iii., 42).

	I.	II.	III.	IV.	Average.
Ratio, Pr_4O_7 : oxalate	58·50	58·56			58·53
Per cent of Pr_2O_3 ..	57·12	57·17			57·15
Per cent of C_2O_3 ..	37·41	37·24	37·17	37·43	37·26
Per cent of H_2O ..	6·42	6·23			6·33
Total..					100·74

$$\text{Ratio, } Pr_2O_3 : 3C_2O_3 = \frac{57·15}{37·26} = 1·5338$$

$$Pr = 141·7 \quad \text{Theoretical} = 140·5$$

The difference between the experimental and theoretical values for the atomic weight of praseodymium may be due to uncertainty either as to the purity of the material employed or as to the composition of the oxide formed by ignition of the oxalate.

A solution of the same praseodymium material containing only a very slight excess of nitric acid was then precipitated by addition to a hot concentrated slightly ammoniacal solution of ammonium oxalate. Precipitation was complete. The precipitate contained very nearly as much ammonia as neodymium oxalate when precipitated under the same conditions.

	I	II.	III.	Average.
Ratio, Pr_4O_7 : oxalate ..	50·48	50·53		50·51
Per cent of Pr_2O_3	49·28	49·33		49·31
Per cent of C_2O_3	38·98	39·01		39·00
Per cent of NH_3	3·45	3·40	3·45	3·43
Per cent of C_2O_3 corresponding to 3·43 per cent of NH_3				7·27
Per cent of C_2O_3 corresponding to Pr_2O_3				31·73

$$\text{Ratio, } M_2O_3 : 3C_2O_3 = \frac{49·31}{31·73} = 1·5541$$

$$M = 143·8 \quad \text{Theoretical} = 140·5$$

The yttrium material employed proved to be far from pure, the atomic weight determined with the precipitate from acid solution being 102·9, while the atomic weight of yttrium is 89·0. Yttrium oxalate was precipitated by adding a solution of a slight excess of oxalic acid to an acid solution of the nitrate, and by adding a nearly neutral solution of the nitrate to a large excess of ammonium oxalate. The precipitate formed in the latter fashion proved to contain considerable ammonia, but when a correction is applied for this ammonia, both precipitates yield nearly the same result for the atomic weight of the sample.

Acid Precipitation.

	I.	II.	Average.
Per cent of Y_2O_3 ..	46·24	46·31	46·28
Per cent of C_2O_3 ..	39·37	39·39	39·38
Per cent of H_2O ..	14·48	14·64	14·56
Total..			100·22

$$\text{Ratio, } M_2O_3 : 3C_2O_3 = \frac{46·28}{39·38} = 1·1750$$

$$M = 102·9$$

Neutral Precipitation with Ammonium Oxalate.

	I.	II.	Average.
Per cent of Y_2O_3	41·22	41·25	41·24
Per cent of C_2O_3	44·84	44·97	44·91
Per cent of NH_3	4·54	4·53	4·54
Per cent of C_2O_3 corresponding to 6·95 per cent of NH_3			9·59
Per cent of C_2O_3 corresponding to Y_2O_3 . ..			35·32

$$\text{Ratio, } M_2O_3 : 3C_2O_3 = \frac{41·24}{35·32} = 1·1671$$

$$M = 102·1$$

The last material investigated was separated from a solution of the rare earths contained in Texas gadolinite by means of fractional precipitation with magnesium oxide. The spectroscope showed it to be rich in erbium, and to contain samarium, while didymium was entirely absent. A portion of the oxalates was soluble in an excess of ammonium oxalate in neutral solution, although in acid solution precipitation was complete, hence undoubtedly ytterbium was present. In order to make certain that the same material was treated both in neutral solution and in acid solution, precipitation with ammonium oxalate in neutral solution was carried out first, and then, after the precipitate had been analysed, the same material was dissolved and precipitated with oxalic acid in the presence of considerable nitric acid.

Acid Precipitation.

	I.	II.	III.	Average
Per cent of M_2O_3.. ..	54·64	54·63	54·63	54·63
Per cent of C_2O_3.. ..	34·94	34·94	34·96	34·95

$$\text{Ratio, } M_2O_3 : 3C_2O_3 = \frac{54·63}{34·95} = 1·5633$$

$$M = 144·9$$

Neutral Precipitation with Ammonium Oxalate.

	I.	II.	Average.
Per cent of M_2O_3 ..	47·88	47·80	47·84
Per cent of C_2O_3 ..	40·05	40·04	40·05

$$\text{Ratio, } M_2O_3 : 3C_2O_3 = \frac{47{\cdot}84}{40{\cdot}05} = 1{\cdot}1945$$

$$M = 105{\cdot}0$$

Per cent of NH_3 (calculated, M = 144·9) .. 4·47

It is interesting to compute the relation of the number of molecules of the oxalates of the rare earths and of ammonia in the precipitates in which the ammonium oxalate content was at a maximum.

	Per cent of oxide.	Per cent of ammonia.	Per cent of $(NH_4)_2C_2O_4$.	Molecules of $(NH_4)_2C_2O_4$ for one molecule $M_2(C_2O_4)_3$.
Nd_2O_3 ..	49·62	3·58	13·05	0·71
Pr_2O_3 ..	49·31	3·43	12·50	0·68
Y_2O_3 ..	41·24	4·53	16·51	0·82
Er_2O_3(?) .	47·84	4·47	16·29	0·93

The extent of the carrying down of ammonium oxalate by the rare earth oxalates which were investigated is much larger than in other cases of occlusion (Richards, *loc. cit.*; Baxter, *Am. Chem. Journ.*, 1902, xxviii., 298), and leads to the conclusion that the real cause of the phenomenon is not the formation of solid solutions of ammonium oxalate in the rare earth oxalates, as is the case with true occlusion, but the formation of a somewhat unstable double salt, possibly of the general formula $M_2(C_2O_4)_3(NH_4)_2C_2O_4$, analogous to the double salts with potassium and sodium oxalates. In either case the extent of the carrying down of ammonium oxalate by the insoluble oxalates would vary with the concentration of the molecular ammonium oxalate at the moment of precipitation.

Summary.

1. The results of the foregoing investigation show that the insoluble oxalates of neodymium, praseodymium, yttrium, and certain other of the rare earths, exhibit a strong tendency to carry down ammonium oxalate, when precipitation takes place in neutral or nearly neutral solution.

2. In the case of neodymium, it is shown that the amount of ammonium oxalate carried down is dependent upon the concentration of molecular ammonium oxalate at the moment of precipitation.

3. Furthermore, it is shown that neodymium oxalate has no tendency to carry down oxalic acid, and that the occlusion of ammonium oxalate may be prevented by diminishing the molecular concentration of ammonium oxalate in solution by means of a strong acid.

It is probable that occlusion by other rare earth oxalates varies in the same way as in the case of neodymium.

4. It is pointed out that the magnitude of the phenomenon is so great that the most reasonable explanation lies in the assumption of the existence of somewhat unstable double salts, rather than of true occlusion.

It seems probable also that the carrying down of the oxalates of sodium and potassium and of the other alkalis will vary with the conditions of precipitation as in the case of ammonium oxalate.

This question is now under investigation in the laboratory (Harvard College).

Ethyl Benzoylglyoxylate.—A. Wahl.—Ethyl benzoylgloxylate is the second known representative of the series of the α-β-diketonic ethers, the other terms being ethyl acetylglyoxylate or ethyl diketobutyrate. It is obtained from ethyl benzoyl acetate by replacing the methylene with the ketone group—

$C_6H_5—CO—CH_2—COOC_2H_5 \rightarrow$

$\rightarrow C_6H_5—CO—CO—COOC_2H_5$.

It reacts with hydroxylamine chlorhydrate to give a monoxime, which is identical with ethyl iso-nitrosobenzoylacetate, showing that only the α-carbonyl has entered into the reaction. This, and other reactions, have served to determine its constitution.—*Comptes Rendus*, cxliv., No. 4.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

FOURTH PAPER.—THE ANALYSIS OF COBALTOUS CHLORIDE.

By GREGORY PAUL BAXTER
and
FLETCHER BARKER COFFIN.

SOME years ago the atomic weight of cobalt was investigated in the Chemical Laboratory of Harvard College by the determination of the ratios of cobaltous bromide to silver and to silver bromide (Richards and Baxter, *Proc. Am. Acad.*, 1897, xxxiii., 115), and of cobaltous bromide (*Ibid.*, 1899, xxxiv., 351), cobaltous chloride and cobaltous oxide (*Ibid.*, 1899, xxxv., 61) to cobalt. From these investigations the probable value for the atomic weight of cobalt was found to be 58·895 (Ag = 107·930), the most satisfactory results being obtained through the analysis of cobaltous bromide.

The determination of the cobalt in cobaltous chloride was effected by reduction of the salt in a current of hydrogen. The salt was not obtained in a state of absolute purity, and it was necessary to apply corrections for the impurities, so that at the time very little value was attached to the result, 59·072.

(The value found from two analyses was 59·044, upon the assumption that the atomic weight of chlorine is 35·456, Ag = 107·930. Recent determinations in the Chemical Laboratory of Harvard College by Richards and Wells ("Publications of the Carnegie Institution," No. 28, 1905) have shown that the value of the latter constant is as high as 35·473. This change in the atomic weight of chlorine produces an increase in the atomic weight of cobalt of 0·028).

In the present investigation it has been found possible with the help of the newly available quartz apparatus to prepare the salt in a state of greater purity, and the analysis of this new material confirms satisfactorily the previous analyses of cobaltous bromide, as well as the doubt concerning the earlier results with the chloride.

Purification of Materials.

Cobaltous Chloride.—The simplest method of freeing cobaltous salts from the salts of other metals was previously found to be precipitation of purpureo-cobalt chloride. This substance is only slightly soluble in cold hydrochloric acid solutions, but readily soluble in hot ammonia. It was prepared by bubbling air for several days through an ammoniacal solution of commercial cobalt chloride, and then adding hydrochloric acid in excess. The purpureo-chloride thus precipitated was collected and the mother-liquor removed as completely as possible by filtration upon a large porcelain Gooch crucible. It was then dissolved in hot re-distilled ammonia, and the solution was filtered into a concentrated, distilled hydrochloric acid solution. The product, after washing with hydrochloric acid, was collected upon a Gooch crucible as before.

The final purification consisted in re-crystallising the amine three times by solution in the purest re-distilled ammonia in a platinum dish, and filtration with a platinum funnel into a quartz dish containing hydrochloric acid which had been distilled with a quartz condenser. Care was taken always to have an excess of acid in the quartz dish, while the acid solution was never allowed to come in contact with platinum since it probably contained free chlorine. The product of the third precipitation was dried on a steam-bath, and was then converted into cobaltous and ammonium chlorides by heating to about 200° in a quartz crucible in an air-bath. For the latter purpose platinum proved to be unsuited, since it was slightly attacked during the decomposition of the amine, while the quartz crucible remained unchanged in weight. A temperature high enough to fuse the amine was very carefully

* From the *Journal of the American Chemical Society*, xxviii., No. 11

avoided. The ammonium chloride still contained by the cobaltous chloride was eliminated during the final heating of the salt in a current of hydrochloric acid gas. During this final heating also care was taken to increase the heat very gradually, so as to avoid fusion of the salt and consequent possible enclosure of ammonium chloride in masses of fused cobaltous chloride (*Zeit. Phys. Chem.*, 1903, xlvi., 194). Cobaltous chloride prepared in this way was designated Sample I.

For preparing the second sample of cobaltous chloride, cobaltamine, which had been at least once dissolved in ammonia and re-precipitated with hydrochloric acid, was heated on a steam-bath with an excess of sulphuric acid, until all chlorine and hydrochloric acid had been expelled. The cobaltous sulphate thus formed was then dissolved in water, the solution was filtered, and a large excess of ammonia was introduced. In order to free the cobalt from alkalis and silica this ammoniacal solution was then electrolysed in a platinum dish, a platinum wire serving as anode, and the dish as cathode. The deposit of cobalt was washed thoroughly with pure water, and dissolved in hydrochloric acid which had been freshly distilled through a quartz condenser. The solution was next evaporated to crystallisation, and the product was twice re-crystallised. In the third crystallisation the salt was drained with a centrifugal machine in which platinum Gooch crucibles served as baskets and platinum crucibles as receivers. Any trace of sulphate occluded by the electrolytic metal was effectually eliminated in this way, for the mother-liquors from the second re-crystallisations when tested for sulphates, always yielded negative results.

After superficial moisture had been eliminated in a desiccator over potassium hydroxide, the salt was powdered in an agate mortar, and heated in a platinum dish in an air-bath to expel the water of crystallisation. The first molecules of water are lost below 50°, and by keeping the temperature below this point it was possible to avoid melting the salt. It has been pointed out by Richards (*Zeit. Phys. Chem.*, 1903, xlvi., 194) that a salt dried in this way is left in the form of a skeleton which allows the escape of vapour from its inmost recesses, while if fusion takes place during drying, a portion of the original salt may be so enclosed within an impervious coating of anhydrous salt that escape of water is impossible. Except in Analyses 3 and 11 the remaining water of crystallisation was expelled during the final heating of the cobaltous chloride in a stream of dry nitrogen and hydrochloric acid gases. Here also the temperature was at first so low that melting of the salt was completely avoided. The temperature was raised to 400° only after apparently all the water was expelled. In Analyses 3 and 11 all the water was expelled in the air-bath.

Silver.—Pure silver was prepared in the fashion usually employed in this laboratory as follows:—To a dilute solution of silver nitrate an excess of hydrochloric acid was added. The silver chloride was shaken many times with pure water and was then reduced to metallic silver by means of a solution of sodium hydroxide and invert sugar. After the metal had been thoroughly washed with water, it was fused on charcoal with a blowpipe, and the lumps of silver were cleaned by scrubbing with sand and etching with nitric acid. Next they were dissolved in re-distilled nitric acid, the excess of nitric acid was neutralised with re-distilled ammonia, and the metal was precipitated with ammonium formate which had been made from re-distilled formic acid. After the silver had been washed with pure water until free from ammonia, it was again fused in a boat of pure lime before a blowpipe. The buttons of silver were then cleaned with nitric acid and washed with water. Finally the silver was deposited electrolytically, the buttons in turn serving as the anode, a piece of the purest silver as the cathode, and a concentrated solution of one of the buttons in nitric acid as the electrolyte. The electrolytic crystals were washed with water and ammonia, dried, and fused in a boat of pure lime in a porcelain tube in a current of electrolytic hydrogen. The ingots were then cut into pieces of convenient size by means of a jeweller's saw, and were subjected to prolonged cleansing with successive portions of dilute nitric acid, until the acid no longer gave a test for iron, traces of which on the surface of the buttons had been introduced from the saw. The pieces were further cleaned with ammonia and with water, dried in air, and then heated to 300° and cooled in a vacuum. They were preserved in a desiccator containing solid potassium hydroxide.

Method of Analysis.

The cobaltous chloride, contained in a platinum boat, was first heated in a current of hydrochloric acid gas in a hard glass tube. An apparatus consisting of a series of towers which supplied either pure dry hydrochloric acid gas, nitrogen, or air was constructed wholly of glass by Dr. M. A. Hines for work upon the atomic weight of cadmium (Baxter and Hines, *Journ. Am. Chem. Soc.*, 1905, xxvii., 222; Baxter, Hines, and Frevert, *Ibid.*, 1906, xxviii., 770) and manganese (Baxter and Hines, *Ibid.*, 1906, xxviii., 1560), and was kindly loaned for this investigation. The hydrochloric acid gas was generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid, and was dried by passing through five towers filled with beads moistened with concentrated sulphuric acid. Nitrogen was produced by passing a mixture of air with an excess of ammonia over heated rolls of copper gauze. It was freed from ammonia and further purified by passing through three wash-bottles containing dilute sulphuric acid, a tower filled with beads moistened with a solution of silver nitrate to remove sulphur compounds taken from rubber connections at the beginning of the apparatus, a tower filled with solid potassium hydroxide, then through three towers filled with beads moistened with concentrated sulphuric acid, and finally through a tube containing re-sublimed phosphorus pentoxide. The air was purified by passing through a tower filled with solid potassium hydroxide, then through four towers filled with beads moistened with concentrated sulphuric acid, and finally through a tube containiug phosphorus pentoxide.

In preliminary experiments in which cobaltous chloride was fused in an atmosphere of pure hydrochloric acid gas, the platinum boat containing the salt was always seriously alloyed on the surface with metallic cobalt. This phenomenon was probably due to partial dissociation of the cobaltous chloride vapour which was invariably formed in considerable quantities when the salt was heated barely to fusion. It was possible to reach a temperature of 400° without meeting the above difficulty, consequently this temperature was employed in the preparation of all samples for analysis, although the salt was not fused at this temperature.

The salt was heated very gently at first in a current of hydrochloric acid gas containing a small quantity of nitrogen until the greater part of the ammonium chloride or water had been expelled, without melting the salt. Then the temperature was increased until finally the salt was maintained at about 400° for at least an hour, usually much longer. After the heating had ceased, the mixture of nitrogen and hydrochloric acid was displaced by nitrogen, and this in turn by dry air, and the boat was transferred to a weighing-bottle without exposure to moist air by means of the bottling apparatus which has frequently served for a similar purpose in many atomic weight investigations in this laboratory (Richards and Parker, *Proc. Am. Acad.*, 1896, xxxii., 59).

The weighing-bottle containing the boat and salt was weighed, after it had stood in a desiccator beside the balance case for some time. Then the boat was transferred to a flask containing about 250 cc. of pure water, and the weighing-bottle was rinsed with water, the rinsings being added to the solution in the flask. A trace of insoluble matter was collected by filtering the solution through a tiny filter into a glass-stoppered precipitating flask, and the filter was ignited in a weighed platinum crucible. This residue, which consisted chiefly of cobalt oxide, never

amounted to as much as two-tenths of a mgrm. In Analyses 1, 2, 9, and 10 a slight increase in the weight of the boat was caused by incipient dissociation of the salt and alloying of the boat. The increase was only 0·05 mgrm. in the case of Analyses 1 and 9, 0·66 mgrm. in the case of Analyses 2 and 10. In these cases the weight of the boat after solution of the cobaltous chloride in water, washing and drying at 100° was determined and used in the calculations. These two analyses yielded results essentially identical with the remainder.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 17th, 1907.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

(Concluded from p. 69).

14. "*The Condensation Products of Triacetic Lactone with Aceto-acetic Ester and β-Aminocrotonic Ester.*" By FREDERICK NOEL ASHCROFT FLEISCHMANN.

Triacetic lactone condenses in presence of strong sulphuric acid and hydrochloric acid, &c., with aceto-acetic ester, to form a *pyrone-lactone*, $C_{10}H_8O_4$, melting at 214°. The substance is extremely stable towards acids, but unstable in presence of alkalis, with which it forms deep yellow solutions. It yields a stable *bromo*-compound (m. p. 190°) crystallising from benzene with benzene of crystallisation, and a *nitro*-derivative (m. p. 200° approx.) which on treatment with strong aqueous ammonia yields aminodehydracetic acid. An unstable abnormal *barium* salt was also prepared, from which an insoluble, unstable *silver* and a *mercuric* salt were obtained.

A similar condensation takes place between triacetic lactone and β-aminocrotonic ester in presence of sulphuric, hydrochloric, or glacial acetic acids. The same pyrone-lactone is produced and, in the last instance, a second compound corresponding to the formula $C_{16}H_{19}O_6N$, the constitution of which is proved by its yielding the ethyl ester of ψ-lutidostyrilcarboxylic acid on treatment with alcoholic potash.

15. "*Derivatives of Multivalent Iodine.* Part II. *Action of Heat on p-Iodoacetophenone Dichloride, p-Iodoacetanilide Dichloride, and on the Dichlorides derived from o-, m-, and p-Iodotoluene.*" By WILLIAM CALDWELL and EMIL ALPHONSE WERNER.

One of us (Werner, *Trans.*, 1906, lxxxix., 1632) has shown that *p*-iodoacetophenone dichloride and *p*-iodoacetanilide dichloride when heated decompose with probable formation of substitution derivatives, thus differing from the general decomposition which has been hitherto recognised in connection with the chlorides derived from tervalent iodine.

When *p*-iodoacetophenone dichloride, $CH_3{\cdot}CO{\cdot}C_6H_4{\cdot}ICl_2$, is heated (Werner, *Trans.*, 1906, lxxxix., 1632) it decomposes suddenly at 93—94°, only traces of chlorine (0·43 per cent) being evolved in the free state, and *chloro-p-iodoacetophenone* is produced to the extent of 98 per cent of the theoretical, thus:—

$$CH_3{\cdot}CO{\cdot}C_6H_4{\cdot}ICl_2 = CH_2Cl{\cdot}CO{\cdot}C_6H_4I + HCl.$$

It forms long, slender prisms (m. p. 126—127°), and on oxidation it furnishes *p*-iodobenzoic acid. With chlorine it yields $CH_2Cl{\cdot}CO{\cdot}C_6H_4{\cdot}ICl_2$, which decomposes at 128—130° with production of *dichloro-p-iodoacetophenone*, $CHCl_2{\cdot}CO{\cdot}C_6H_4I$ (m. p. 62—63°). This also gives *p*-iodobenzoic acid on oxidation, and unites with chlorine to form $CHCl_2{\cdot}CO{\cdot}C_6H_4{\cdot}ICl_2$, which is decomposed by heat with evolution of most of the chlorine in the free state.

p-Iodoacetanilide dichloride, $CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}ICl_2$, decomposes at 105°, and yields *chloro-p-iodoacetanilide*, $CH_2ClCO{\cdot}NH{\cdot}C_6H_3ClI$ (m. p. 144°), from which a *chloro-iodoaniline*, $C_6H_3ClI{\cdot}NH_2$ ($NH_2:I:Cl = 1:4:2$ or 3) (m. p. 73°), is obtained. The *picrate* melts at 132°.

Chloro-*p*-iodoacetanilide unites with chlorine, forming $CH_3CO{\cdot}NH{\cdot}C_6H_3Cl{\cdot}ICl_2$, which decomposes at 131°, and yields a substitution product which has not yet been investigated.

The action of heat on the chlorides of *o*-, *m*-, and *p*-iodotoluenes, prepared by Willgerodt, has been examined.

o-Tolyliodochloride decomposes at 85—86°, and yields *o*-iodobenzyl chloride, $C_6H_4I{\cdot}CH_2Cl$, which gives *o*-iodobenzoic acid on oxidation.

m-Tolyliodochloride decomposes at 88°, giving an iodochloride which yields on oxidation an acid melting at 210°, and containing both chlorine and iodine.

p-Tolyliodochloride decomposes at 110°, giving *p*-iodobenzyl chloride. In each case a small proportion of the original iodotoluene is regenerated.

16. "*Disalicylamide.*" By JAMES MCCONNAN.

o-Salicylsalicylamide does not possess the properties previously attributed to it (*Patentschrift*, No. 111, 656); the compound thus named by Cohn was probably disalicylamide.

Under suitable conditions *o*-salicylsalicylamide rearranges, forming disalicylamide, and *vice versâ*; this is another case of the metoxazone tautomerism peculiar to acyl derivatives of salicylamide, and already studied in the cases of the benzoyl and the acetyl derivatives (McConnan and Titherley, *Trans.*, 1906, lxxxix., 1318).

17. "*Benzoyl Derivatives of N-Methylsalicylamide.*" By JAMES MCCONNAN and MORRIS EDGAR MARPLES.

N-*N*-Dimethylsalicylamide is a stable substance; *N*-methyl-*N*-benzoylsalicylamide, however, is unstable, and under the conditions of its formation it is either instantly hydrolysed or rearranges, forming *N*-methyl-*O*-benzoylsalicylamide. It thus appears that, although derivatives of the general formula $C_6H_4{<}^{OH}_{CO{\cdot}N{\cdot}R_2}$ are stable, substances of the type $C_6H_4{<}^{OH}_{CO{\cdot}N{\cdot}R{\cdot}Ac}$ are too unstable to permit of isolation. This result is of considerable interest, since McConnan and Titherley have already shown (*Trans.*, 1906, lxxxix., 1327) that *N*-*N*-diacylsalicylamides, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}N{<}^{R}_{R}$, are too unstable to exist.

18. "*The Velocity of Reaction of Bromine with some Unsaturated Acids in Aqueous Solution.*" By ERNEST BARRETT and ARTHUR LAPWORTH.

Recent communications from W. Herz and B. Mylius (*Ber.*, 1906, xxxix., 3816) and from J. J. Sudborough and J. Thomas (*Proc.*, 1906, xxii., 318) deal with the addition of bromide to cinnamic acid and its esters in organic solvents. We have been engaged in the examination of addition of bromine to some unsaturated acids in aqueous solutions in the hope of throwing some light on the mechanism of such reactions.

The changes are somewhat difficult to follow, as the velocities are very considerable, and even in dilute solutions the time must be measured in seconds instead of hours. The temperature employed was 14·9° in the first three cases and 25·5° with the monobromocinnamic acids, and the experiments were carried out in artificial light.

Cinnamic Acid.—With equimolecular proportions of acid and halogen in N/1000 solutions, nearly the whole of the bromine disappeared in thirty seconds. With excess of bromine, 1·5 mols. were absorbed in about eighty minutes, this effect being due to the formation of bromocinnamic acids from the initial product. With crotonic acid and bromine, in equimolecular proportions in N/200 solutions, more than nine-tenths of the bromine was used in forty-five seconds.

Benzylidenemalonic Acid.—With N 200 solutions, about 0·5 mol. of bromine was absorbed in one minute, and the change had during the greater part of its course the form of a termolecular reaction. With the sodium salt the velocity is much greater, nine-tenths of the bromine disappearing in about thirty seconds. In N/2 sulphuric acid the velocity was about one-tenth of its usual value. Potassium bromide also lowers the reaction velocity, but not so decidedly; thus in N/2 potassium bromide the velocity was about three-fifths of its ordinary value.

The reaction, towards its end, is complicated, the product losing hydrogen bromide and carbon dioxide, the resulting bromocinnamic acid accounting for some of the bromine. Thus with excess of bromine, 1½ mols. of halogen disappeared in twenty minutes.

β-Monobromocinnamic Acid.—With equimolecular proportions of acid and bromine in N 100 solutions, about 0·25 mol. of bromine disappeared during the first half-minute. The change, in presence of excess of hydrogen chloride or potassium chloride, is of the bimolecular form; in absence of these agents the decomposition of the initial addition product occurs with measurable speed. The sodium salt is brominated at about the same rate as the free acid at first, but later the secondary reactions are more evident. Hydrogen chloride or potassium bromide diminish the reaction velocity, but apparently never to more than half the normal value. In this case, mineral acids have considerably less effect than have bromides, an observation consistent with the fact that the sodium salt and the acid have nearly the same velocity of bromination. The sodium salt of the stereoisomeric *α-monobromocinnamic acid*, it is interesting to note, absorbs bromine many times more rapidly than does the free acid.

The results appear inconsistent with the view that bromine dissociates into ions before addition at a double linking. They seem to show, however, that the ions of the acids, as well as the acids themselves, unite with bromine directly.

19. "*Note on the Molecular Complexity of Liquids.*" By Albert Ernest Dunstan and Ferdinand Bernard Thole.

In a recent paper (*Trans.*, 1906, lxxxix., 1774) Holmes deals with the question of molecular complexity from the point of view of the volume changes produced on mixing. By calculating the greatest difference between the volume of alcohol actually present and the volume which would be present assuming no contraction, he assumes, for mixtures of alcohol and water, for example, that this maximum ($1C_2H_5{\cdot}OH,1H_2O$) implies approximation of the ratio of the radii of "influential spheres" to unity.

The following table shows that the ratio does not approximate to unity, taking as a basis of calculation the true molecular volumes given by the author:

	Mol. vol.	Max. diff. of alcohol percentages by vol. at ·	Above ratio of radii
Ethyl alcohol ..	3·22	$C_2H_5{\cdot}OH,1\frac{1}{2}H_2O$	$\sqrt[3]{3{\cdot}22}/1 = 1{\cdot}47$
n-Propyl alcohol	4·07	$C_3H_7{\cdot}OH,1\frac{1}{2}H_2O$	$\sqrt[3]{4{\cdot}07}/1 = 1{\cdot}60$
Propionic acid..	4·06	$C_2H_5{\cdot}CO_2H,1H_2O$	$\sqrt[3]{4{\cdot}06}/1 = 1{\cdot}59$
n-Butyric acid ..	5·08	$C_3H_7{\cdot}CO_2H,1H_2O$	$\sqrt[3]{5{\cdot}08}/1 = 1{\cdot}72$

Throughout the paper the author refers to the one constituent of a mixture as possessing the more active molecule usually of greater molecular volume and carrying a preponderating effect into the mixture. It would be more correct to look upon solution from the point of view of the reciprocal effect of the one component on the other; when this is done, for example, in the case of alcohol and water, the maximum effects are to be noticed at the proportions $1C_2H_5{\cdot}OH,3H_2O$ (Dunstan, *Trans.*, 1904, lxxxv., 823).

Holmes regards the lower alcohols and acids of the paraffin series, from similar considerations, as having the same complexity as water; water he assumes to have the aggregate formula $(H_2O)_2$. Now there is a considerable amount of evidence available which shows that the earlier liquids of homologous series tend to associate somewhat particularly those the members of which are hodroxylated.

It has been shown that the quantity $\frac{\text{Viscosity}}{\text{Mol. vol.}} \times 10^6$ is nearly constant, viz.: 60 for such liquids as are currently accepted as unimolecular, but for the hydroxylated associated class the values are much in excess of 60 (Dunstan, *Zeit. Physikal. Chem.*, 1905, li., 732):

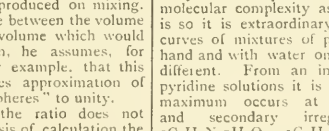
Benzene	65
Chloroform	67
Carbon disulphide	60
Water	193
Methyl alcohol	138
Ethyl alcohol	189
Acetic acid	195
Glycerol	106,000

Again, when viscosity coefficients are plotted against molecular weights, not only do the alcohols and acids relatively stand apart from the unimolecular liquids, but also the curves show such divergences at the beginnings of the series as to justify the idea of increased association.

Glycerol and nicotine are the only unimolecular liquids quoted in the table (p. 1785); now glycerol is not only notably viscous, but also has a remarkably high temperature coefficient of viscosity; both these facts indicate its association.

Carbon disulphide (*loc. cit.*) is mentioned as possessing four times the complexity of alcohol and is therefore represented by the formula $[CS_2]_8$; it is inconceivable from such data as, for example, its low boiling point, its low viscosity coefficient, the variation of its molecular surface energy with temperature, and its position in the molecular weight-viscosity chart.

Pyridine is quoted as a liquid which has the same molecular complexity as water and the alcohols. If this is so it is extraordinary that the viscosity concentration curves of mixtures of pyridine with alcohol on the one hand and with water on the other should be so entirely different. From an investigation now in progress on pyridine solutions it is found that in aqueous solution a maximum occurs at the proportions $2C_5H_5N,5H_2O$, and secondary irregularities at $3C_5H_5N,2H_2O$, $2C_5H_5N,7H_2O$, $1C_5H_5N,5H_2O$, and $1C_5H_5N,10H_2O$. These discontinuities can only be explained by the assumption of loosely held complexes in dynamic equilibrium, which ionise to a considerable extent, and which generally behave like ammonium hydroxide,



but in alcoholic solution no maximum point is noted; the curve is composed of two branches which represent (1) the viscosity curve of associated alcohol with dissociated pyridine, and (2) dissociated alcohol with associated pyridine.

A precisely similar curve is afforded by alcohol benzene mixtures. A study of the viscosity curves (Dunstan, *Trans.*, 1905, lxxxvii., 11, and *loc. cit.*) enables the changes in association which take place to be followed qualitatively, whilst the curves connecting molecular weight with viscosity coefficient give a quantitative idea as to the degree of association existing in any given liquid

Anniversary Dinner.

It has been decided by the Council to arrange for a Dinner of the Fellows of the Society and their friends on Friday, March 22nd, 1907, this being the day fixed for the Annual General Meeting. Further particulars will be announced shortly.

FARADAY SOCIETY.

Ordinary Meeting, January 29th, 1907.

Prof. H. E. ARMSTRONG, F.R.S., in the Chair.

Discussion on "Osmotic Pressure."

THE discussion was opened by the EARL of BERKELEY, who exhibited and described his Apparatus for the Direct Measurement of Osmotic Pressure.

The ordinary direct method of measuring osmotic pressures is to obtain equilibrium on the two sides of the semi-permeable membrane by means of the pressure of a head of liquid. The method devised by the author and Mr. E. G. J. Hartley substitutes mechanical pressure, which is put straight on the solution, and equilibrium thus obtained. Reversing the usual arrangement, the solution is put outside the semi-permeable tube, in an outer containing tube of gun-metal, and the solvent inside, suitable mechanical arrangements being provided for rendering the joints leak-tight. The pressure is obtained from a plunger worked with a pile of weights and delivered through a mercury U-tube to the solution outside the septum. Equilibrium is obtained or calculated by watching through a telescope the motion of the solution in a gauge. The measurements may be made at any desired temperature. Corrections are applied for the imperfect semi-permeability of the membrane by analysing the solvent to see if any solution has passed into it.

A vapour-pressure method for measuring osmotic pressure was also described. This is a modification of the Ostwald and Walker dynamical method. Air is sucked through a spiral train of glass vessels containing first sulphuric acid, to dry it, then the solution from which it gets saturated up to the vapour pressure of the latter, then the solvent, of which it here takes up more, and finally sulphuric acid again. There are two trains of vessels arranged to oscillate about a central axis, so that the air does not actually bubble *through* the liquids, which is unsatisfactory, but merely passes *over* them, glass beads being placed in the tubes to increase the melting surfaces. The whole apparatus can be placed in a bath and worked at any desired temperature. Arrhenius's relation was used for calculating the osmotic pressures from the lowered vapour pressures, and very concordant results were shown to have been obtained between measurements made by the direct-pressure and the vapour-pressure methods. The author is of opinion that the latter method will chiefly have to be relied upon to furnish accurate data for the further study of osmotics.

Mr. W. C. DAMPIER WHETHAM, F.R.S., speaking on "Indirect Methods of Measuring Osmotic Pressure," agreed as to the importance of the vapour-pressure method. He discussed the formula used by Berkeley and Hartley, and explained the difference between it and and the van't Hoff formula obtained from thermodynamic considerations, the expressions being identical where there is no change of volume of the solvent as it enters the solution.

Dr. T. M. LOWRY spoke on "Osmotic Pressure from the Standpoint of the Kinetic Theory." The motion of the particles postulated by the kinetic theory leads in the case of composite gases or liquids to a process of diffusion. When diffusion is resisted a pressure is set up which constitutes the osmotic pressure of the system. This can be effected by means of a semi-permeable membrane, through which only one of the constituents can pass. Such membranes undoubtedly act in virtue of their solvent properties.

The application of the equation $PV = RT$ to the osmotic pressure of gases could be predicted on general theoretical grounds, but there was no *à priori* reason for supposing that it would be applicable to the case of liquids. The mere fact that all liquids were not miscible was sufficient to show that the conditions were widely different from those prevailing in mixed gases. The validity of the law had been established experimentally, and must be accepted as a fact of fundamental importance in all discussions as to the nature of osmotic pressure.

In the early years of the osmotic discussion it had been assumed by van't Hoff and others that since osmotic pressures and gas pressures could be calculated by means of the same formula the conditions must be identical in the two cases, and it was definitely stated that in dilute sugar solutions the osmotic pressure was wholly due to the bombardment of the membrane by the molecules of the sugar, the effects produced by the water molecules being substantially identical on either side of the membrane. The alternative view, that osmotic pressure represented a diminution in the activity or "active mass" of the solvent was suggested by Poynting in 1896, and had subsequently been advocated by Armstrong, Beilby, van Laar, and others. In most cases it had been assumed that the essential factor was a diminution in the average energy of the water molecules. From the standpoint of the kinetic theory this was unnecessary, as also was the view advocated by Rodger and by Traube that the solute was directly combined with one or more molecules of the solvent. The mere presence in the surface of the solution of molecules of the solute which could not enter the membrane was sufficient to check the escape of solvent particles from the solution into the membrane, without affecting the reverse passage of solvent from the membrane into the solution. This would lead to a diminished solubility on the side of the solution and to a flow of liquid through the membrane which could only be checked by putting pressure on the solution.

The simplest case of a semi-permeable membrane is undoubtedly to be found in the surface of separation between liquid and vapour. At such a surface the kinetic theory postulates a continual interchange of molecules between the two phases. But whilst the rate of escape or evaporation would be reduced by the presence of non-volatile molecules in the surface, the rate of condensation would be unaffected, and equilibrium could only be restored by decreasing the vapour pressure and so diminishing the rate of condensation at the surface of the solution. In this case a quantitative relationship could be deduced. If N and n were the relative numbers of particles of solvent and solute in the surface and p and p^1 the vapour pressures of solvent and solution, then if each molecule of solute replaced a single molecule of solvent in the surface layer, the reduction of vapour pressure would be shown by the equation—

$$\frac{p^1}{p} = \frac{N}{N+n}.$$

It had been shown by Nernst that from this simple relationship the identity of the osmotic pressure of a dilute solution with the pressure exerted by a gas of equal molecular concentration could be directly deduced. The blocking of the surface was, therefore, sufficient to afford, not merely a qualitative, but also a quantitative explanation of osmotic pressure.

The further discussion of the surface structure of liquids as related to the osmotic phenomena will be printed in the *Transactions*.

Professor L. KAHLENBERG sent in a communication to the discussion on "The Bearing of Actual Osmotic Experiments upon the Conception of the Nature of Solutions."

The occurrence of osmosis and its direction and extent are determined by the nature of the septum and of the

liquids that bathe it. Experiments have shown, too, that there is always a major and minor current present, following in opposite directions, although it often appears as if the osmotic process were one-sided. In this case the septum is termed "semi-permeable," and recent research has centred around so-called semi-permeable membranes which really do not exist. The author has demonstrated that it is peculiarly strong selective action on the part of the septum which causes it to be approximately semi-permeable in certain cases, and he has recently even succeeded in separating two colloidal substances by dialysis. This selective action is due to the solubility or insolubility of the substances concerned in the membrane, and therefore osmotic pressure is due to the same forces—essentially chemical in character in the opinion of the author—as the process of solution, and they may be quite variable as different septa and different liquids are employed. The usually accepted "sieve theory" is untenable, because larger molecules frequently go through a membrane more readily than smaller molecules.

So-called semi-permeable membranes have of late years been studied on account of their bearing on van't Hoff's "gaseous pressure" theory of solution and of osmotic pressure. This maintains that as long as the membrane is semi-permeable the osmotic pressure is the same in the case of any septum for a given solution against the pure solvent, a position contrary to experimental facts.

Again, by applying Carnot's cycle and the usual thermodynamic formulæ to the hypothetical case of abstracting, and then returning solvent from a dilute solution in a cylinder fitted with a semi-permeable piston, relations have been deduced between latent heats of fusion and freezing points, and latent heats of vaporisation and boiling points, assuming the gas equation to hold for dilute solutions. But the results obtained are frequently far from the experimental values found for different solutes in the case of one and the same solvent (in the case of electrolytes), and it has been necessary to postulate either dissociation or polymerisation; but the author referring to his previous papers, considers these explanations are weak and unnecessary. The thermodynamic calculations involve the assumption of a semi-permeable membrane which at the same time is quite passive. As it is selective action which produces semi-permeability, no such membrane can exist. Therefore, thermodynamic osmotic pressure (which is not really osmotic pressure at all) is quite a different thing from that measured by experiment. Finally, to speak of the experimental osmotic pressure of any solution, without mentioning what septum is used to separate that solution from what other liquid, is devoid of meaning.

Mr. H. N. Morse communicated tables containing a summary of the recent experiments, the results of which are about to be published, made by him and Mr. Frazer, with glucose and cane-sugar. The conclusions arrived at are:—1. In the vicinity of 20° the osmotic pressure exerted by either is equal to that which a molecular equivalent quantity of a gas would exert if its volume were reduced, at the same temperature, to the volume of the solvent in the pure state. 2. Between 18° and 26°, at which the measurements were made, both cane-sugar and glucose in solution are in the anhydrous condition. Measurements made just above 0° yield pressures somewhat above the calculated gas pressures. Measurements with electrolytes are about to be made in which osmotic pressure and dissociation will be determined simultaneously.

Dr. J. C. Philip thought, with reference to Dr. Lowry's hypothesis, that whatever views might be entertained as to the nature of osmotic pressure, one was bound, on thermodynamic grounds, to conclude that dilute solutions must behave as a gas in relation to concentration and temperature.

Mr. J. G. A. Rhodin remarked on the fact that osmotic pressure as usually explained seemed to work in the wrong direction, namely, from the lower in the direction of the higher pressure. It was remarkable, too, that a semi-permeable membrane should conduct electricity so easily. Many of the supposed agreements between calculated and observed results and modern physical chemistry were due to a reckless and unjustifiable use of the method of least squares.

Dr. Alexander Findlay said that on account of unfamiliarity with van't Hoff's theory of solutions there had been much misunderstanding as to what was the problem actually to be investigated. Referring to Kahlenberg's objection to semi-permeable membranes, from the thermodynamic standpoint it did not matter whether there were selective absorption or not, provided the changes in energy were equal in opposite directions. He considered that the quantitative side and the thermodynamic side of the subject had been thoroughly worked out, and the remarkable accuracy of the work of Morse and Frazer, and Berkeley and Hartley, pointed to absolute agreement between experiment and the van't Hoff thermodynamic theory. He did not take kindly to Dr. Lowry's kinetic explanation, and thought that the membrane might be left out altogether, and the diffusion only between a solution and a layer of pure solvent on the top of it made use of for explaining what took place.

Mr. W. A. Davis said that van't Hoff's original hypothesis neglected the influence exerted on the solute by the solvent; Dr. Lowry's modification of van't Hoff's conception was therefore necessary from that standpoint. Osmotic pressure had also been explained as the tendency to equalise the surface tension on the two sides of the osmotic cell.

The Earl of Berkeley disagreed with Dr. Findlay that the thermodynamic was the only logical way of looking at things. He discussed further the discrepancy between the formula used by him and the thermodynamic formula which could be explained on the conception one formed of osmotic pressure.

Dr. T. M. Lowry said that the views he advocated accounted for the negative direction of the osmotic flow referred to by Mr. Rhodin. It was not remarkable that Boyle's law should hold good for osmotic pressure, but it was remarkable that the constant R in the two cases should be identical. The agreement should throw light on the surface structure of liquids.

The Chairman emphasised the general applicability of the vapour-pressure method, which, although tedious and troublesome, could be used with any solvent, at all temperatures, and under all pressures. The compressibility of liquids would prevent it agreeing quite with direct measurements; it was therefore important that careful comparisons of the two should be made. In reply to Dr. Findlay, Morse and Frazer's results did not agree with those of Berkeley and Hartley; there was a possible constant error in the former, in spite of the extraordinary accuracy of the work. He hoped more experimental work would be done with living tissues on the line of Pfeffer's original measurements. The term "osmotic pressure," unless merely used in the sense of a pressure required to establish equilibrium, was a misleading one; there was nothing to show that a pressure existed inside a solution in a closed vessel apart from simple gravity pressure. The results of Morse and Frazer brought dilute and concentrated solutions into line, and were a great advance on the van't Hoff treatment; they put the ordinary gas point of view quite out of court. He deprecated the dogmatic, unscientific treatment to which the whole subject had been subjected for the purpose of bolstering up a particular point of view: the facts needed examination from a broad and critical standpoint.

NOTICES OF BOOKS.

Practical Sanitation. By George Reid, M.D., D.P.H. Thirteenth Edition. London: Charles Griffin and Co., Ltd. 1906.

A great deal of useful information with which householders and the general public would do well to acquaint themselves, is contained in this handbook, which treats fully of such questions as the filtration of water for drinking purposes, the ventilation and warming of dwelling houses, schools, and other places, and infection and the most effectual ways of disinfecting. The primary object of the author was, however, to provide a handbook for the use of sanitary inspectors, and this aim he has admirably fulfilled. His advice and teaching are sound, and no branch of sanitation is passed over. An appendix by Dr. Herbert Manley on Sanitary Law gives a summary of the chief provisions of the various statutes affecting the duties of inspectors, a knowledge of which is now necessary for candidates for the certificates of the Sanitary Inspectors' Examination Board and of the Royal Sanitary Institute. The thirteenth edition has been published very soon after the appearance of the twelfth, in order that recent progress in sanitation may be described, and the appendix has been entirely re-written.

A Handbook of Physics and Chemistry. By Herbert E. Corbin, B.Sc. (Lond.), M.R.C.S., L.R.C.P., D.P.H., and Archibald M. Stewart, B.Sc. (Lond.), B.A. (T.C.D.). London: J. and A. Churchill. 1907.

This book contains a complete elementary course of physics, inorganic and organic chemistry, such as is indicated by the syllabus for the First Examination of the Royal Colleges and also those of the Pharmaceutical Society and the Royal Veterinary College, and candidates for these examinations will find it convenient to have all that they require in one text-book, written specially to meet their needs. The subjects are treated from a theoretical point of view, and while there is not much that is new in the book the explanations are always clear and concise. In the third edition chapters on light and sound have been added, and some of the section on inorganic chemistry has been enlarged.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 4, January 28, 1907.

Cuprous Metaphosphate.—V. Auger.—On heating copper filings in a platinum crucible with phosphoric acid, no marked change in the metal takes place until the acid is converted into a mixture of pyro- and metaphosphoric acids. Hydrogen is evolved, and the acid turns brown with the formation of the cuprous salt, but this is at the same time oxidised by the air, and bluish white crystalline scales of cupric metaphosphate are formed. To avoid the action of the air and obtain the lower salt, metaphosphoric acid heated to a dull red is poured upon excess of copper filings in a covered platinum crucible; heating is continued for a time, and the dark mass is then rapidly decanted into another platinum crucible, which is immediately covered. Analysis shows that the cuprous phosphate, stable at a red heat, on cooling decomposes into cupric metaphosphate and metallic copper. Thus, $Cu_2(PO_3)_2 = Cu(PO_3)_2 + Cu$. It is possible to obtain the cuprous salt and keep it in the cold state for several days, if the hot solution is allowed to fall, a drop at a time, into methyl chloride. Perfectly transparent little glassy masses are thus obtained of a pale yellow colour, composed of cuprous metaphosphate in solution in metaphosphoric acid. They can be preserved for several days in a sealed tube, but a slow molecular change takes place, and the transparency gives place to an opaque red-brown appearance, due to deposition of metallic copper. This decomposition of the cuprous salt into the cupric salt and the free metal is observable with a variety of acids. In spite of their instability, the cuprous salts of organic acids have, under certain conditions, been obtained and analysed.

Solubility of Carbon in Barium Carbide and Strontium Carbide.—H. Morel Kahn.—The author has made quantitative investigations of the solubility of carbon in the carbides of barium and calcium similar to those he has previously made in the case of calcium carbide, under differing conditions, in the electric furnace. The carbides of strontium and barium are made under the same conditions as that of calcium, but they are produced at lower temperatures, and therefore the heating of the carbides in the charcoal crucible is made less intense by placing the latter in a larger crucible and filling the space between the two with lamp-black. The following results were obtained at a constant intensity of 550 to 600 ampères, under about 90 volts:—

	Time of heating.	Graphite per cent.
	I. *Barium Carbide.*	
1.	6 minutes	1·25, 1·50
2.	7 ,,	2·25
3.	8 ,,	2·77
4.	9 ,,	3·30, 3·90
5.	10 ,,	4·20, 4·30
6.	11 ,,	5·40, 6·20
	II. *Strontium Carbide.*	
1.	6 minutes	1·30, 1·50
2.	7 ,,	2·10, 2·28
3.	8 ,,	2·75, 3·20
4.	9 ,,	4·45
5.	10 ,,	6·15, 6·25

Thus, the carbides of the alkaline earths appear to possess in common the property of dissolving carbon. It is not possible to increase indefinitely the proportion of carbon dissolved, and a temperature is soon reached beyond which no comparable results are obtained. Prolonged heating causes dissociation and vaporisation of the carbide.

Causes which Influence the Estimation of Fluorine in Mineral Waters.—P. Carles.—There has been much conflicting evidence from skilful chemists as to the presence or absence of fluorine in certain mineral waters, the explanation being, perhaps, that the presence of silica, often in considerable quantity, renders the research on the fluorine in the evaporated residue of the water uncertain. It is therefore a question of successful elimination of the silica, and whether the acid method or the alkaline method is preferable. From a mineral water said to contain no fluorine, positive results were obtained by treating with sodium bicarbonate and ammonium carbonate successively, filtering off the precipitate of silica, and adding potassium acetate, barium chloride, and hydrochloric acid to the filtrate. A precipitate containing fluorine was thus obtained. No fluorine being obtained when the evaporated mineral water residue is treated with acid probably means that the fluorine has been eliminated as hydrofluoric acid. The following conclusions were drawn from researches by the alkaline method:—1. Out of ninety-three specimens of natural mineral waters, the presence of fluorine is pretty general, since only four or five gave negative results. 2. The degree of alkalinity of the water appears to bear some relation to the weight of fluorine separated. 3. Calcium fluoride dissolves or precipitates in the water according to the quantity of carbonic acid gas present.

A New Method of Estimating the Halogens in Organic Compounds by Means of the Metal-ammoniums.—E. Chablay.—It has been found in studying the action of the metal-ammoniums upon different organic compounds containing halogens, that all the halogen corresponding to the quantity of matter employed is recovered always as the alkaline halogen salt. The author has made use of this property to obtain the estimation of these elements in bodies belonging to different series. *Principle of the Method.*—On treating with sod-ammonium or potassium-ammonium one molecule of any organic compound containing one or more atoms of a halogen, the latter is completely removed by the alkali metal of the ammonium, giving the corresponding halogen salt. This is easily estimated volumetrically by a silver nitrate solution. The results obtained from a great variety of experiments prove that this method is as accurate as the classical methods with calcium carbonate, or with the sealed tubes of Carius, the latter method involving well known inconveniences. The method here described presents no difficulties, since the reactions are carried out in open tubes and at low temperatures; it is also more rapid, admitting of five or six estimations in a day; finally, it is of very general application, even for gaseous bodies such as methyl chloride.

Condensed Chromic Sulphates.—Albert Colson.—The researches of M. Recoura have shown that, on boiling, violet solutions of chromium sulphate turn green, owing to a condensation expressed as follows:—

1. $2Cr_2(SO_4)_3 + H_2O = H_2SO_4 + Cr_2O(SO_4)_5$. The same reaction applies to chrome-alum and the normal green salts, as already announced by the author. The pentasulphate, $Cr_4O(SO_4)_5$, is found to exhibit the same property, but this is not easily identified, because boiling water is capable of reacting upon the pentasulphate, setting free a new quantity of acid:—

2. $Cr_2O(SO_4)_5 + H_2O = Cr_3O_2(SO_4)_4 + H_2SO_4$. *Interpretation of Results.*—According to the views of M. Mathias, there occurs an association of a number of sulphuric molecules twice as great in the green salt as in the violet salt, *i.e.*, two violet chromic molecules condense in one molecule of the green sulphate. The green sulphate may be written $SO_4=Cr-SO_4-Cr=SO_4$ (with $|$ $|$). As the divalent radical, SO_4, changes under the action of water into two monovalent radicals, HSO_4 and OH, the above representation indicates the existence of a classs of dichromic salts, of which the author believer other types exist in the concentration of the normal green salts.

Some Derivatives of Hordenine.—E. Léger.—In consequence of the fact that hordenine possesses the functions of both a tertiary amine and a phenol, it is able to give derivatives of both these classes. Derivatives of the amine function may be salts or alcohol derivatives. Those of the phenol function may be ether-salts or ether-oxides. The following derivatives are described:—1. *Derivatives of the Amine Function.*—The neutral tartrate of hordenine, $(C_{10}H_{15}NO)_2,C_4H_6O_5$; the acid tartrate, $C_{10}H_{15}NO.C_4H_6O_5$; chloromethylate of hordenine, $C_{10}H_{15}NO.CH_3Cl$; chloroethylate, $C_{10}H_{15}NO,C_2H_5Cl$; bromoethylate, $C_{10}H_{15}NO,C_2H_5Br$; iodoethylate, $C_{10}H_{15}NO,C_2H_5I$. II. *Derivatives of the Phenol Function*, obtained by the action of the corresponding acid chlorides upon hordenine, in solution in pyridine, in the case of the ether-salts. The chlorhydrate of benzoylhordenine, $C_{10}H_{14}(C_7H_5O)NO.HCl$; the bromhydrate,—

$$C_{10}H_{14}(C_7H_5O)NO.HBr;$$

the cinnamylhordenine; the chlorhydrate of cinnamylhordenine, $C_{10}H_{13}(C_9H_7O)NO,HCl + H_2O$; the chlorhydrate of anisylhordenine, $C_{10}H_{13}(C_8H_7O_2)NO,HCl + H_2O$. III. *Derivatives of Both Functions.*—1. Sulphomethylate of hordenine,—

$$C_{10}H_{15}\overset{CH_3}{\underset{SO_4CH_3}{N}}O + NaI = C_{10}H_{15}\overset{CH_3}{\underset{I}{N}}O + SO_4CH_3Na.$$

2. Iodomethylate of methylhordenine, produced according to the above equation, may be written—

$$C_6H_4\begin{cases}CH_2-CH_2-\overset{CH_3}{\underset{I}{N}}(CH_3)_2.\\OCH_3\end{cases}$$

Acetyl Nitrate.—Amé Piclet and Eugène Khotinsky.—The authors have obtained the new compound acetyl nitrate, $CH_3-COO-NO_2$, by dissolving in the cold nitric anhydride in acetic anhydride,—

$$CH_3-CO\rangle O + \begin{matrix}NO_2\\NO_2\end{matrix}\rangle O = 2CH_3-CO-O-NO_2.$$

This can only be separated from the active anhydride by fractionating under reduced pressure. It passes over at 22 under a pressure of 70 mm.; it is a colourless liquid, very mobile, very hygroscopic, giving off copious vapours in air, which explode with violence when rapidly heated. The latter property prevented analysis by combustion, and an indirect method was resorted to for determination of the composition, the body being dissolved in water, the total acids determined by titration, and the nitric acid by Kjeldahl's method. Acetyl nitrate reacts with alcohols to give their acetic ethers or their nitric ethers, according to the nature of the alcohol and the temperature. With the aromatic compounds, it has a strongly nitrating action, its activity being due to the fact that the reaction occurs without elimination of water,—

$$R-H + NO_2-O-COCH_3 = R-NO_2 + CH_3COOH.$$

It reacts thus with benzene, toluene, anthracene, thiophene below 0°.

MEETINGS FOR THE WEEK.

TUESDAY, 19th.—Royal Institution, 3. "The Visual Apparatus of Man and Animals," by Prof. William Stirling.

—— Faraday Society, 8. "Present Position and Future Prospects of the Electrolytic Alkali and Bleach Industry," by J. B. C. Kershaw.

WEDNESDAY, 20th Society of Arts, 8. "Cold Storage and Food Supply," by Hal Williams.

—— Microscopical, 8. "An Early Criticism of the Abbe Theory," by J. W. Gordon. "Some Tardigrada of the Sikkim Himalaya," by J. Murray. "Some Rhizopods from the Sikkim Himalaya," by Dr. E. Penard. An Exhibition of Slides of Marine Zoological Objects lent by Mr. Flatters.

THURSDAY, 21st.—Royal Institution, 3. "The Minute Structure of Igneous Rocks and their Significance," by Mr. A. Harker.

—— Chemical, 8.30. "Constitution of Oxyazo Compounds," by W. B. Tuck. "Influence of Solvents on the Rotation of Optically Active Compounds—Part IX. A New General Method for Studying Intramolecular Change," by T. S. Patterson and A. McMillan. "The Reduction Products of Ortho and Para-Dimethoxybenzoin," by J. C. Irvine and A. M. Mondie. "Replacement of Halogens by Hydroxyl—I. The Hydrolytic Decomposition of Hydrogen and Sodium Monochloroacetates by Water and by Alkali, and the Influence of Neutral Salts on the Reaction Velocities," by G. Senter. "The Reaction of Ammonium Salts with the Constituents of the Soil," by A. D. Hall and C. T. Gimingham.

FRIDAY, 22nd.—Royal Institution, 9. "Flame in Gas and Petrol Motors," by Dugald Clerk.

—— Physical, 5. "Transformer Indicator Diagrams," by Prof. Lyle. "Ionisation of Gases by α-Particles of Radium," by Prof. Bragg. "A Micromanometer," by B. Roberts.

SATURDAY, 23rd.—Royal Institution, 3. "Rontgen, Cathode, and Positive Rays," by Prof. J. J. Thomson.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2465.

THE TECHNICAL ESTIMATION OF ANTIMONY AND ARSENIC IN ORES, &c.

By A. H. LOW.

The technical estimation of antimony in ores containing also arsenic and possibly tin is frequently a tedious and more or less unsatisfactory operation. Distillation methods may give correct results, but considerable experience in their manipulation is usually required, and perhaps, also, special apparatus not always at the disposal of the technical chemist having only an occasional antimony determination to make. The following method for both antimony and arsenic is free from these objections, and, in my laboratory, has given results closely checking those obtained by distillation. While it is largely based upon old ideas there are some points of novelty that tend to expedite the work, and the method as a whole is different from any I have seen published. The time required for determining both antimony and arsenic in an ore need not exceed two and one-half hours.

Take 1 grm. of the ore in a 150 cc. flask, add 7 grms. of potassium acid sulphate, 0·5 grm. of tartaric acid, and 10 cc. of strong sulphuric acid. Heat over a free flame (manipulating the flask in a holder), cautiously at first, finally with the full power of a Bunsen burner, until any free sulphur is entirely expelled and the separated carbon is completely oxidised, leaving a clean mass or melt with but little free sulphuric acid. Allow to cool with the flask on its side, as otherwise the solidifying cake may break it, or, spread the melt around on the sides while cooling. The object of the tartaric acid in the decomposition is to reduce the arsenic and antimony to the *ous* condition, thus rendering the subsequent solution of the antimony easy and the precipitation of both metals as sulphides rapid and complete. A covered casserole may be employed instead of a flask, if considered more convenient.

After cooling, add 50 cc. of water, 10 cc. of strong hydrochloric acid, and 2 or 3 grms. of tartaric acid. Heat nearly to boiling for a short time to dissolve everything soluble (especially anhydrous iron sulphate), but do not actually boil for fear of volatilising some arsenic. Filter, washing with hot water. This filtration is advisable but not a necessity. Dilute the filtrate to about 300 cc. with hot water, maintain the liquid warm, and pass in hydrogen sulphide. The arsenic and antimony being in the *ous* condition are quickly precipitated, ten minutes being usually sufficient. Filter, washing with hydrogen sulphide water. Rinse the sulphides into a beaker with hot water, using as little as will suffice, add a little colourless potassium sulphide and warm to extract the arsenic and antimony sulphides (also tin sulphide, if present). (If sodium sulphide is used a separation of sodium chloride crystals, occluding a little antimony, may occur later). Pour through the last filter and wash with warm water containing a little colourless potassium sulphide. With small amounts of other sulphides present one extraction will usually suffice. Receive the filtrate in a 300 cc. flask. Add to it about 3 grms. of potassium acid sulphate and 10 cc. of strong sulphuric acid and boil the mixture, finally over a free flame, until the free sulphur is all expelled and the greater part of the free acid also. Allow the clear melt to cool with the flask on its side. When sufficiently cool add 25 cc. of water and 10 cc. of strong hydrochloric acid and warm to effect complete solution, then cool nearly to room temperature under the tap. Now add 40 cc. of strong hydrochloric acid and pass in hydrogen sulphide. The arsenic will be quickly precipitated, being in the *ous* condition. Filter, washing flask and precipitate with a mixture of 2 volumes strong hydrochloric acid and 1 volume of water. Before filtering, moisten the filter with the acid mixture. A double filter supported by a platinum cone will not break under very gentle suction.

The arsenic is now all on the filter and the antimony (together with any tin) in the filtrate. Determine the two metals as follows:—

Antimony.—Dilute the filtrate with double its volume of warm water and pass in hydrogen sulphide. Filter the antimony sulphide and wash with hydrogen sulphide water sufficiently to remove most of the hydrochloric acid. Rinse the sulphide from the filter into a beaker, add a little ammonium sulphide, and warm to effect solution. Pour through the last filter, and wash with water containing a little ammonium sulphide. Receive the filtrate in a 300 cc. flask. Small amounts of antimony sulphide may be dissolved directly on the filter. To the filtrate add about 3 to 4 grms. of (pure) potassium acid sulphate and 10 cc. of strong sulphuric acid. Boil as previously described to expel, first the water, then all the free sulphur and finally most of the free acid. Cool, add 50 cc. of water and 10 cc. of strong hydrochloric acid. Heat to effect solution and then boil for a few minutes to expel any possible sulphur dioxide. Finally, add 10 cc. more of strong hydrochloric acid, cool under the tap, dilute to about 200 cc. with cold water, and titrate with a standard solution of potassium permanganate. The solution ordinarily used for iron titrations will answer. Tin, if present, exists as stannic sulphate and is without influence. The oxalic acid value of the permanganate multiplied by 0·9532 will give the antimony value.

Arsenic.—Thoroughly wash out the hydrochloric acid from the sulphide with hydrogen sulphide water, also rinsing out any sulphide remaining in the flask. Dissolve the sulphide (this may usually be done on the filter) in warm ammonium sulphide solution, and wash with the same solution diluted. Receive the filtrate in a 300 cc. flask. Add 2 to 3 grms. of potassium acid sulphate and 5 cc. of strong sulphuric acid. Evaporate, boiling to a small bulk, and then manipulate the flask over a free flame until the sulphur is entirely expelled and most of the free acid also. Take up, after cooling, by warming with 50 cc. of water and then boil sufficiently to expel any possible sulphur dioxide. Now drop in a bit of litmus paper as an indicator and then add ammonia until the solution is slightly alkaline. Again acidify slightly with hydrochloric acid and cool to room temperature. Finally add 3 to 4 grms. of sodium acid carbonate and a little starch liquor and titrate with standard iodine solution. Pay no attention to a slight discoloration toward the end, but proceed slowly until a single drop of the iodine produces a strong permanent blue colour.

The iodine solution may be prepared by dissolving about 11 grms. of iodine in a little water with the addition of about 20 grms. of potassium iodide and diluting to 1 litre. Standardise with arsenious oxide. Dissolve about 0·150 grm. in 5 cc. of strong hydrochloric acid by warming very gently, dilute and neutralise as described above, and finally titrate with the iodine solution. One cc. of the latter will equal about 0·003 grm. of arsenic.

It is perhaps unnecessary to enumerate a long list of instances showing the accuracy of the above method, and I will therefore mention only the following:—

	Taken. Grm.	Found. Grm.
As	0·0792	0·0798
Sb	0·0534	0·0531
Sb	0·0516	0·0514
Sb	0·0521	0·0525

With an oxidised ore: As, 0·568 per cent; Sb 0·106 per cent. Repeat: Sb, 0·106 per cent.

On this ore Pearce's method (modified) gave As 0·57 per cent.

The same ore gave, by Knorr's distillation method, Sb 0·082 per cent.

Ledoux and Co., of New York, reported Sb 0·081 per cent.

Mr. R. L. Wilder, of El Paso, tested this ore by the new method and found Sb 0·1005 and 0·0802 per cent. —*Journal of the American Chemical Society*, xxviii., No. 12.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

FOURTH PAPER.—THE ANALYSIS OF COBALTOUS CHLORIDE.

By GREGORY PAUL BAXTER
and
FLETCHER BARKER COFFIN.

(Concluded from p. 78).

Method of Analysis (continued).

FROM the corrected weight of cobaltous chloride very nearly the requisite quantity of pure silver was calculated. This silver was weighed out, and dissolved in re-distilled nitric acid diluted with an equal volume of water in a small flask provided with a column of bulbs to prevent loss by spattering. After the solution had been diluted with an equal volume of water, the nitrous fumes were expelled by gentle heat. Then the solution of silver nitrate, after dilution until its concentration was about 1 per cent, was poured slowly, with constant agitation, into the solution of cobaltous chloride, which also had been diluted to a like concentration in the precipitating flask, and the flask was shaken for some time. The precipitation and subsequent filtration of the silver chloride were carried out in a cupboard made of ruby glass.

After the solution had stood for about two days with occasional agitation, and after the supernatant liquid had become perfectly clear, 25 cc. portions of the solution were tested with hundredth-normal solutions of silver nitrate and potassium chloride in a nephelometer (Richards and Wells, *Am. Chem. Journ.*, 1904, xxxi., 220) for excess of chloride or silver, and, if necessary, either standard silver nitrate or potassium chloride solution was added, and the process of shaking and testing repeated, until the amounts of silver and chloride were equivalent. The test solutions were always returned to the flask since they contained an appreciable amount of silver chloride, and the weight of silver chloride subsequently obtained was corrected for the quantity thus introduced.

As soon as the exact end-point had been found, about 1 decigrm. of silver nitrate in excess was added, in order to produce as complete precipitation of the silver chloride as possible, and the flask was again shaken and allowed to stand until clear. The precipitate of silver chloride was collected upon a Gooch crucible, after it had been washed several times with a dilute solution of silver nitrate, and finally ten times with pure water. Then it was heated in an electric oven for five hours at 180°, cooled in a desiccator, and weighed.

In order to determine the moisture still retained by the dried silver chloride, in each case it was transferred as completely as possible to a porcelain crucible, and weighed. Then the salt was fused by heating the small covered crucible contained in a large crucible, and again weighed.

Although the filtrate and silver nitrate wash-waters were nearly free from dissolved silver chloride, the aqueous washings contained appreciable quantities of this substance. The amount of dissolved salt in both filtrate and wash-waters was determined by comparison with standard chloride solutions in a nephelometer. It has recently been

* From the *Journal of the American Chemical Society*, xxviii., No. 11.

THE ATOMIC WEIGHT OF COBALT.

$CoCl_2 : 2Ag$.
Cl = 35·473.

Series I. Ag = 107·930.

Number of analysis.	Sample of $CoCl_2$.	Weight of $CoCl_2$ in vacuum. Grms.	Weight of residue. Grm.	Change in weight of boat. Grm.	Weight of silver in vacuum. Grms.	Weight of silver added or subtracted. Grm.	Corrected weight of $CoCl_2$. Grms.	Corrected weight of silver. Grms.	Atomic weight of cobalt.
1	I.	1·09971	0·00007	+0·00005	1·82659	+0·00012	1·09959	1·82671	58·991
2	I.	1·47808	0·00009	+0·00006	2·45404	−0·00006	1·47733	2·45398	59·005
3	II.	3·84144	0·00011	0·00000	6·38106	−0·00025	3·84133	6·38081	59·005
4	II.	3·64357	0·00015	0·00000	6·05223	+0·00009	3·64342	6·05232	58·999
5	II.	2·96330	0·00015	—	4·92221	+0·00023	2·96315	4·92244	58·995
6	II.	3·48435	0·00017	—	5·78776	+0·00039	3·48418	5·78815	58·991
7	II.	3·29530	0·00007	—	5·47391	+0·00019	3·29523	5·47410	58·995
8	I.	1·57670	0·00015	—	2·61889	+0·00016	1·57655	2·61905	58·992
								Average ..	58·997

Series II.

Number of analysis.	Sample of $CoCl_2$.	Weight of $CoCl_2$ in vacuum. Grms.	Weight of residue. Grm.	Change in weight of boat. Grm.	Weight of AgCl in vacuum. Grms.	Loss on fusion. Grm.	Weight of silver. Grms.	Corrected weight of AgCl. Grms.	Atomic weight of cobalt.
9	I.	1·09971	0·00007	+0·00005	2·42529	0·00011	1·82659	2·42676	59·009
10	I.	1·47808	0·00009	+0·00006	3·25929	0·00028	2·45404	3·26095	58·988
11	II.	3·84144	0·00011	0·00000	8·47596	0·00040	6·38106	8·47735	59·014
12	II.	2·96330	0·00015	—	6·53901	0·00035	4·92221	6·54039	58·997
13	II.	3·48435	0·00017	—	7·69032	0·00058	5·78776	7·69284	58·986
14	II.	3·29530	0·00007	—	7·27146	0·00049	5·47391	7·27284	59·004
15	I.	1·57670	0·00015	—	3·47946	0·00032	2·61889	3·48012	58·982
								Average ..	58·997

$CoCl_2 : AgCl$.

Number of analysis.	Sample of $CoCl_2$.	Weight of $CoCl_2$ in vacuum. Grms.	Weight of residue. Grm.	Change in weight of boat. Grm.	Weight of AgCl in vacuum. Grms.	Loss on fusion. Grm.	Weight of AgCl from asbestos. Grm.	Corrected weight of AgCl. Grms.	Corrected weight of AgCl. Grms.	Atomic weight of cobalt.
9	I.	1·09971	0·00007	+0·00005	2·42529	0·00011	0·00016	0·00142	1·09959	2·42676	59·009
10	I.	1·47808	0·00009	+0·00006	3·25929	0·00028	0·00006	0·00188	1·47733	3·26095	58·988
11	II.	3·84144	0·00011	0·00000	8·47596	0·00040	0·00000	0·00179	3·84133	8·47735	59·014
12	II.	2·96330	0·00015	—	6·53901	0·00035	0·00035	0·00121	2·96315	6·54039	58·997
13	II.	3·48435	0·00017	—	7·69032	0·00058	0·00017	0·00093	3·48418	7·69284	58·986
14	II.	3·29530	0·00007	—	7·27146	0·00049	0·00018	0·00169	3·29523	7·27284	59·004
15	I.	1·57670	0·00015	—	3·47946	0·00032	0·00011	0·00087	1·57655	3·48012	58·982
								Average ..			58·997
								Average of Series I. and II. ..			58·997

found in this laboratory by Richards and Stähler that if the solution is made slightly alkaline with ammonia and then is acidified immediately before being tested, more accurate results are obtained (*Am. Chem. Journ.*, 1906, xxxv., 512). This procedure was followed in the greater part of our analyses. The testing took place very shortly after the filtration, so that suspended material had no time to settle.

After the filtrate and wash-waters had been analysed for dissolved silver chloride, they were filtered through a tiny filter to collect a small quantity of asbestos mechanically detached from the Gooch crucible. This filter was washed with ammonia to eliminate the silver chloride, which might have been collected and which had been determined in the nephelometric test, and was ignited in a weighed platinum crucible.

For most of the work a new short-armed Troemner balance, sensitive to a fiftieth of a mgrm. with a load of 50 grms., was used. The gold-plated brass weights were three times carefully standardised to hundredths of a mgrm. and were used for no other work. Weighings were made by substitution with counterpoises as nearly like the objects to be weighed as possible.

In order that the proper vacuum correction for cobaltous chloride might be applied, the density of this substance was determined by Dr. M. A. Hines in connection with similar work upon manganese. The salt was first fused in a platinum boat in a current of hydrochloric acid gas, and then the toluene displaced was determined with a pycnometer previously described (Baxter and Hines, *Am. Chem. Journ.*, 1904, xxxi., 220).

Density of $CoCl_2$. (*Density of Toluene* = 0·86166).

Weight of $CoCl_2$ in vacuum.	Weight of toluene displaced in vacuum.	Density of $CoCl_2$.
Grms.	Grms.	25°/4°.
4·8719	1·2522	3·352
4·6520	1·1991	3·343
	Average ..	3·348 (*a*)

(*a*) Playfair and Joule obtained the value 2·937. Landolt-Bornstein, "Physikalisch-Chemische Tabellen," 3rd Ed., p. 238.

The following vacuum corrections were applied:—Cobaltous chloride, +0·000215; silver, −0·000029; silver chloride, +0·000073.

Evidence of the purity of the silver and of the absence of appreciable occlusion by the silver chloride may be obtained from the relation between the amount of silver used in the titrations and the corresponding amount of silver chloride formed. In all, 29·46524 grms. of silver produced 39·14905 grms. of silver chloride, a ratio of 100·000 to 132·865. Richards and Wells found this ratio to be 100·000 to 132·867.

Attention should be called to the fact that if the salt made from the amine still contained appreciable amounts of ammonium chloride after being heated, the observed value for the atomic weight of cobalt would have been too low. On the other hand, if the cobaltous chloride made from the crystallised salt retained traces of water, the result would have been too high. The average of all the results obtained with salt made from the amine is 58·995, and the average of the results with salt made from the crystallised chloride is 58·998. The very slight difference between these values lies within the experimental error of the determinations. Evidently, the salt was in all cases essentially free both from ammonium chloride and water. The almost complete absence of ammonium chloride was also shown by two experiments in which the amine was heated in a current of hydrochloric acid in the usual manner, and then the salt was dissolved in water, and the cobalt was precipitated by the addition of ammonia-free sodium hydroxide. In one case where 1·76 grms. of cobaltous chloride were used, the filtered solution, when tested with Nessler's reagent, showed the presence of 0·00025 grm. of ammonium chloride, while in the other 2·13 grms. of cobaltous chloride yielded 0·00005 grm. of ammonium chloride. This proportion of impurity would have lowered the observed atomic weight 0·004 in the first case, and only 0·001 in the second. The average 0·003 is exactly the difference between the averages from the two samples of material. If this correction is applied in the analyses where the cobaltamine was used, the averages of both Series I. and Series II. are raised to 58·998, a negligible change.

Whether or not such a correction is applied the average of Series I. and II. confirms very closely the value 58·995 previously found by analysis of the bromide; hence the atomic weight of cobalt may, as before, be assumed to be 59·00 referred to silver 107·930.

We are deeply indebted to the Cyrus M. Warren Fund for Research in Harvard University for many platinum, quartz, and other vessels.

RAPID METHODS FOR THE ESTIMATION OF ROSIN IN PAPER.

By CLAYTON BEADLE.

MANY methods have been proposed for the estimation of rosin in paper, but they are all more or less open to objection. Difficulties in connection with most of these processes I have dealt with in detail in communications to technical journals devoted to paper-making.

There is an objection common to all these processes, particularly when dealing with common papers, namely, that the fibres themselves contain resinous matter, often in sufficient quantity to entirely obscure the actual amount of rosin added for the purposes of sizing. Unfortunately, there is no acknowledged method of distinguishing between rosin added as rosin size and rosin or resinous bodies pre-existing in the fibrous furnish of the paper, particularly when we have regard to the fact that the rosin (colophony), common and natural to the fibres themselves, is, as in the case of chemical and mechanical wood pulp, the same in chemical nature and reactions as the rosin of the rosin-size.

A common method for the qualitative determination of rosin in paper is to boil the paper in absolute alcohol or rectified spirit for a few minutes, cool, and add the alcoholic extract to cold distilled water. If rosin be present, on dilution with water it becomes precipitated, and produces a cloudiness. The extraction is conveniently done on 0·10 grm. of paper in a small test-tube (12 mm. diameter) with 2 cc. of absolute alcohol. This, after cooling, is carefully poured on to the surface of distilled water in a second and similar test-tube filled to within an inch of the top. At the point at which the alcohol and water meet, an opaque ring or layer of precipitated rosin is gradually developed. If a number of papers are under examination and equal weights and volumes be taken, a comparison of the zones after standing four hours gives one a rough idea of the relative proportions of the rosin in each of the samples. If now the liquids are mixed by placing the thumb over the tube and inverting two or three times, and the tubes are chosen of equal diameters; the comparative opacities of the different liquids also gives one a rough and perhaps a more accurate idea of the relative proportions.

Unfortunately, there are occasionally other substances than rosin present in paper and soluble in absolute alcohol, which give also a cloudiness on dilution with water. These substances can, as a rule, be detected and sometimes allowed for. The writer has for a long time made use of a quantitative process based on the above method. The procedure is as follows:—

A standard solution of rosin is made up by dissolving 1 grm. air-dry commercial colophony in 1000 cc. of absolute

alcohol. This is of such a strength that 1 cc. of the standard rosin solution is equal to 1 per cent of rosin on 0·1 grm. of paper. 0·1 grm. of the paper to be examined is cut into small fragments, placed in a small clean test-tube, and 2 cc. of absolute alcohol added. It is raised to boiling, allowed to stand for fifteen minutes, raised again, and the extract decanted into another clean tube. The paper is treated with a second and third quantity of absolute alcohol in a similar manner. The clear extract is cooled to 15° C., and added to a test-tube containing cold distilled water, three parts filled, shaken, and allowed to stand ten minutes. I prefer ordinary test-tubes to Nessler tubes for this purpose. To another test-tube of colourless glass and of exactly the same diameter containing the same volume of water, is added from a burette some of the standard rosin solution in different trial lots, until the exact opacity is matched. In this manner the amount of rosin in some papers can be determined within 0·1 per cent.

The process was tested by a number of blank experiments, using rosin-free filter-paper, to which known percentages of rosin dissolved in alcohol had been added. The opacity increases somewhat on standing, so that a few minutes must be allowed before final reading. It is also found necessary to add the standard rosin all at once.

A usual method for the determination of rosin in paper is to place, say, from 2 to 5 grms. of paper in a Soxhlet, exhaust with alcohol, and weigh the residue in a flask in the usual manner.

The author has proved by a number of careful experiments, the results of which have already been published in detail, that the results obtained by this method are not so satisfactory as those obtained by the volumetric method above described, as they include other substances soluble in alcohol which do not give a precipitate on the dilution of water. Moreover, there are almost always substances extractable by alcohol contained even in the purest bleached cotton and linen fibres; these we find are seldom below 0·4 per cent

There are other methods, one of which is based upon the saponification of rosin by boiling with aqueous soda and its subsequent precipitation with acid, and its determination either volumetrically or gravimetrically. Such processes are unsatisfactory on account of removal by soda or other substances such as lignin, particularly in papers containing lignified fibres such as jute and mechanical wood.

It remains but to refer to attempts made by the author to utilise the Raspail reaction, both for the qualitative and quantitative estimation of rosin in paper. A number of experiments made by partially immersing strips of paper of known composition in strong sulphuric acid show that the pink coloration could not be relied upon as an indication of the presence of rosin when the paper consisted of impure celluloses, but when pure it is useful as a check test.

Having devised a volumetric process for the quantitative estimation of rosin in paper, it becomes necessary to distinguish between the rosin or resinous bodies natural to the fibres, and the rosin added as rosin-size to the paper. The distinguishing feature between these two conditions of the rosin is to be found in the fact that resinous bodies natural to the fibre do not produce a sizeing effect. The author has examined an adaptation of Hertzberg's method on the lines recommended by Mr. James Strachan, and has found it to be very useful as a guide, particularly when done in conjunction with foregoing volumetric method.

The evidence as to the presence of rosin in the process about to be described is chiefly based upon the difference in sizeing effect in the paper before and after the removal of the rosin by treatment with ether. The principle of this spot test with ether can be explained in a few words. If a drop of ether be applied to paper sized with rosin, the rosin is dissolved. If the ether be allowed to evaporate very slowly the dissolved rosin will be restored to the fibres of the paper again; in other words, the distribution of the rosin will be the same as before the spot of ether had been applied. If, however, the ether is rapidly evaporated the rosin will form a ring or fringe round the edge of the drop, leaving the interior of the drop in a more or less unsized condition. The same condition of affairs can be exemplified by placing two drops of brine on the surface of the blotting paper—one of which is evaporated slowly and the other quickly. That which evaporates rapidly forms a crystalline fringe round the edge, whereas the slow evaporation will give rise to crystals distributed all over the surface.

J. Strachan's method of applying Hertzberg's ether test is as follows:—

On the exact spot on the sample to be tested a small cross mark is made with a pencil, so that the spot to which the ether is applied may be at once located. The paper is then rolled or bent slightly in the two directions of the sheet, so that the surface presents a slightly hollow appearance. This is done for the reason that on a convex or even flat surface ether spreads rapidly, but when carefully applied to a slightly concave surface the tendency to spread is checked very considerably. The paper is then warmed by simply holding it four or five inches above a wire gauze resting on a tripod stand, under which is placed a small Bunsen burner. While in this position ether is applied from a small pipette (preferably 5 cc. capacity) containing about ten drops, whilst the finger is pressed against the top of the pipette. It should be done at such a distance that the warmth of the hot air rising from the burner is just sufficient to expel the ether very gently and in fairly large drops. For some papers a single drop is enough. It is generally advisable to apply two or more drops, taking care that the second is applied just before the first is completely evaporated, and so on. In some samples, however, five or six drops are required to sufficiently develope the ring of resin. The ring appears quite distinctly at first (immediately after test), but after an hour or so it fades somewhat. For this fading we have not at present formed an explanation. After the test is applied the paper is examined in a good light. If resin be present it shows as a very narrow dark coloured zone fringing the edge of the spot, *i.e.*, where the ether evaporated most quickly. The central portion within this zone, in the case of a white paper, presents a whiter appearance by reflected light than the rest of the sheet. By transmitted light the reverse is the case, because this portion having most of the rosin abstracted from it becomes more opaque than the rest of the sheet, whilst the zone of rosin, which is the darkest portion of the sheet by reflected light, becomes the most translucent by transmitted light. In a quick test, after application of the ether, the rosin zone is best revealed by holding the paper between the light and the observer.

When the rosin-ring is somewhat faint, Strachan combines another of Hertzberg's tests with the one above referred to, viz., the tannic ether ferric chloride test, with the result that an almost invisible ring is instantly developed: this, if done with care, is very striking.

The ferric chloride is applied with a pen in the manner prescribed by Hertzberg, and the ether solution of tannic acid is applied to the other side of the paper with a glass rod. By transmitted light the portion deprived of rosin is black, the rosin ring fairly clear, and that portion outside the ring is more or less blackened according to the degree to which the paper is sized with rosin, and the strength of the applied solutions, &c. A 1 per cent aqueous solution of tannic acid may be used instead of the ether solution, but the ethereal solution is to be preferred.

The substitution of alcohol for ether is not to be recommended, chiefly on account of the slower evaporation of the former, and, as already pointed out, rapid evaporation is essential for the production of a satisfactory zone of resin.

It is found convenient to apply the ferric chloride solution with a fine pointed gold pen. The test may be quickened and simplified in various ways, such as by taking a narrow strip of the sample to be tested, folding it one end so as to form a V-shaped hollow, the paper being

held by the unfolded end. Into the V-shaped end the drops of ether are applied at a spot about 15 mm. from the free end, whilst the strip is held in a horizontal position. The ether is applied drop by drop over a Bunsen flame, as above described. A glass tube drawn out to a fine orifice is dipped into Stephens' blue-black ink, and drawn lightly over the surface and parallel with edge of the strip. As it passes over the treated portion, it will be noticed that on the untreated part the ink stands upon the surface, but immediately sinks into the middle of the spot, and refuses entirely to penetrate the point where the line of ink intersects the fringe of deposited rosin.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

By ARTHUR A. NOYES and WILLIAM C. BRAY.

Introduction.—Outline of the Investigation.

This investigation was undertaken for the purpose of studying the processes of qualitative analysis in general use, with reference to their effectiveness in enabling small quantities of each of the more common elements or element-groups to be detected in the presence of any of the other elements, and for the purpose of selecting the methods best adapted to this end and of improving them wherever desirable and practicable. In spite of the vast number of text-books on qualitative analysis in which more or less different processes are recommended, there seems to have been made in recent years no exact systematic study of the relative effectiveness of the separations or of the delicacy of the final tests. It has seemed to us, therefore, worth while to make a detailed investigation of this kind; and as a result of it to develop, if possible, a system of analysis which will enable a quantity of any element as small as one or two mgrms. to be detected in any mixture. Effort will also be made to employ only such processes as enable a rough estimate to be made of the quantity of the various elements present; for this is usually a more important function of a good qualitative analysis than the mere determination of their presence or absence. To this end tests of excessive delicacy, like certain colour reactions, will be avoided, and each element will be obtained in the solid form as a precipitate or residue, as far as possible.

Especial attention will also be devoted to the chemical reactions involved in the process and to the explanations of them furnished by the Mass-Action Law and Ionic Theory. Since the first systematic application of modern theories to analytical chemistry was made by Ostwald, many physico-chemical researches have been published which make it possible to give such explanations with certainty in a greater number of cases. References to the more important articles relating to the chemistry of the processes and to their theoretical interpretation will be given.

The elements and element-groups included in this system of analysis are primarily those which, with remarkable unanimity, are treated of in the ordinary schemes of qualitative analysis, but we have also introduced the more important of the so-called rare elements, in so far as this has seemed practicable without seriously complicating or modifying the process best adapted to the more common elements. An independent "System of Qualitative Analysis Including nearly all the Metallic Elements" is also being worked out in the Laboratory of Physical Chemistry, Massachusetts Institute of Techology; and parts of it have already been published under this title in the *Technology Quarterly*. The latter scheme differs from the one here presented in that the detection of the rare elements forms the essential feature, instead of a merely incidental one.

The results will be presented in the form that seems best adapted to the purposes of the analyst. The "System of Analysis" is for convenience in publication primarily divided into a series of parts, each of which treats of one of the large divisions of the subject. Under each part is first presented a "General Discussion," in which are given the reasons for the adoption of the process employed. This is followed by a "Tabular Outline," which gives a survey of the important steps and the chemical reactions involved in the process of analysis. Then comes the chapter entitled "Procedures and Notes," in which the details of the process are presented and discussed. Next are given the "Test Analyses," which were made with known mixtures in order to test the efficiency of the process. Finally are presented "Confirmatory Experiments and References," which serve to substantiate the statements made in the notes and to justify the details of the procedures.

In the procedures the operations are described in much detail; it is, however, assumed that the analyst is familiar with the manipulative processes of exact qualitative analysis and with the ordinary precautions for assuring completeness of precipitating, washing, &c. In the notes are explained the purposes of the operations and the specific chemical reactions involved from the point of view of the Mass-Action Law and the Ionic Theory, with the general principles of which the reader is assumed to be acquainted. The directions are almost always given in the form applicable to the case where all elements that might be present are present, the modifications admissible when certain operations lead to negative results being usually sufficiently evident. The scheme consists of a series of numbered "Procedures," a new one being begun whenever the substance has been resolved into two parts (such as a precipitate and filtrate) which are to be submitted to different operations. Procedures which are devoted to the detection or separation of the rarer elements are preceded by an asterisk, and are further designated by a letter attached to the procedure number; they may be omitted if such elements are not to be tested for. Notes under other procedures, when they relate to such elements, are also distinguished by an asterisk. At the beginning of each procedure the one by which the substance was last treated, and at the end of each procedure those by which the two separated portions of it are next to be treated, are referred to by number.

Most of the experiments described under "Confirmatory Experiments and References" are undoubtedly merely confirmations of previously known chemical facts. The application of these facts to the specific conditions of the procedures it was, however, constantly necessary to test; and it has seemed worth while to make the results a matter of record. The experiments are preceded by a reference to the procedure and note to which they relate.

Of the abbreviations employed only a few need be explained:—G. D. is used for General Discussion; P., for Procedure; N., for Note; C. E., for Confirmatory Experiments; T. A., for Test Analyses. A number within parentheses expresses the specific gravity at 15°. When it is directed to add a variable quantity of a reagent (for example, 5—15 cc.), the amount used should be adjusted to the size of the precipitate or residue.

The metallic elements have been classified in "Groups" on the basis of their behaviour toward the general ("group") reagents, and these groups are designated and defined as follows, the rarer elements here considered being indicated by an asterisk:—*Silver group*, elements precipitated wholly or in part by hydrochloric acid (Ag, Pb, Hg [mercurous], *Tl); *copper group*, elements precipitated by hydrogen sulphide from weakly acid solution whose sulphides remain undissolved in large quantity by yellow ammonium sulphide (Hg [mercuric], Pb, Bi, Cd, Cu, *Au, *Pt); *tin group*, elements precipitated by hydrogen sulphide from weakly acid solution whose sulphides dissolve readily or in considerable quantity in yellow ammonium sulphide (As, Sb, Sn, *Au, *Pt, *Se, *Te, *Mo); *iron group*, elements not precipitated by hydrogen sulphide from acid solution, but precipitated by ammonium

* From the *Technology Quarterly*, xix., No. 3, September, 1906.

hydroxide and sulphide (Co, Ni, Fe, Mn, Cr, Al, Zn, *Ti, *Zr, *U, *V, *Be); the *alkaline-earth group*, elements not precipitated by any of these reagents, but precipitated by ammonium carbonate (Ba, Sr, Ca); the *alkali group*, elements not precipitated by any of the preceding reagents (Mg, Na, K, *Li).

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 7th, 1907.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MR. H. S. REDGROVE was formally admitted a Fellow of the Society.

The PRESIDENT gave expression to the deep sense of loss experienced by Fellows of the Society through the death, on February 2nd, of Professor Dmitri Ivanovitsch Mendeleeff, F.R.S., and of Professor Nicolai Menschutkin, which occurred on February 5th. These chemists were Honorary and Foreign Members of the Society, having been elected in 1883 and 1898 respectively.

Certificates were read for the first time in favour of Messrs. John Campbell Allan, 91, Norse Road, Scotstoun, Glasgow; Francis James Bailey, Findon Hill, Sacriston, Durham; Charles Stanley Gibson, B.A., 45, Shakespeare Street, Manchester; Joshua Craven Gregory, B.Sc., F.I.C., 126, Woodlands Road, Glasgow; John Robinson, Agricultural College, Aspatria, Cumberland.

Of the following papers, those marked * were read:—

*20. "*The Rapid Electro-analytical Deposition and Separation of Metals.* Part I. *The Metals of the Silver and Copper Groups and Zinc.*" By HENRY JULIUS SALOMON SAND.

The experiments on a new electro-analytical method of rapid determination and separation of metals referred to in a preliminary note (*Proc.*, 1906, xxii., 43) have been continued. The metals hitherto studied are silver, mercury, copper, bismuth, lead, cadmium, and zinc. With the exception of the separation silver-mercury, each metal has been successfully separated from all the others by the method of graded potential. In order to separate silver from mercury the metals were deposited together, converted into their cyanides, and these separated in the usual way by means of their different behaviour to acids. The silver was then estimated electrolytically in the pure silver cyanide obtained. Experiments have been carried out in which the seven metals studied have been quantitatively separated from one solution. The silver was separated from the mercury as described above, and the lead and part of the bismuth were removed on the anode. All the other separations were brought about by graded potential. The metals were deposited in the following sequence:—1. Mercury and silver. 2. Lead and part of bismuth on anode; copper and rest of bismuth on cathode. 3. Cadmium. 4. Zinc. 5. After dissolving the combined deposit of copper and bismuth, the latter was estimated. 6. Rest of bismuth separated from lead after dissolving the deposit. 7. Lead. 8. Cadmium tested for traces of lead. One evaporation was necessary. The time required for the depositions in these experiments varied between five and fifteen minutes.

DISCUSSION.

Mr. EDWARD GARDNER asked if the author had had any experience in depositing copper from solutions containing a large quantity of ferric sulphate, and whether he had been able, in such solutions, to obtain an adherent deposit by any method of graded potential.

Mr. SAND stated that the presence of metals of variable valency, such as iron, which pass from one stage of oxidation to another with extreme readiness, caused much difficulty. Work on such cases was being carried out at present.

*21. "*The Alkaloids of Ergot.*" By GEORGE BARGER and FRANCIS HOWARD CARR.

The authors assign to Tanret's crystalline ergotinine the formula $C_{35}H_{39}O_5N_5$, and have abandoned the formula $C_{28}H_{32}O_4N_4$, provisionally suggested in a preliminary note communicated to the British Association (CHEMICAL NEWS, 1906, xciv., 89). Tanret's original formula, $C_{35}H_{40}O_6N_4$, was based on faulty nitrogen determinations. In the above mentioned note, the authors suggested the name ergotoxine for a second amorphous ergot alkaloid, of which they had crystallised several salts. Subsequently, this alkaloid was described by Kraft (*Arch. Pharm.*, 1906, ccxliv., 336) as hydroergotinine, because by boiling its solution in methyl alcohol it was converted into ergotinine. Kraft did not analyse hydroergotinine.

In an attempt to acetylate ergotoxine with acetic anhydride the authors obtained ergotinine. As the latter alkaloid contains no acetyl group the change must be due to dehydration. The reverse change occurs when an ergotinine solution in dilute phosphoric acid is boiled. The crystalline phosphate of an amorphous alkaloid is then formed, closely resembling ergotoxine phosphate.

For ergotoxine the formula $C_{35}H_{41}O_6N_5$ is deduced from the analyses of the free base and of the following crystalline salts:—

$C_{35}H_{41}O_6N_5,HCl$, m. p. 205°; $C_{35}H_{41}O_6N_5,H_3PO_4,H_2O$, m. p. 186—187°; $C_{35}H_{41}O_6N_5,C_2H_2O_4$, m. p. 179°; and $(C_{35}H_{41}O_6N_5)_2,C_2H_2O_4$, m. p. 179°.

The two formulæ, $C_{35}H_{39}O_5N_5$ and $C_{35}H_{41}O_6N_5$, thus independently arrived at for the crystalline and the amorphous alkaloid respectively, establish the theory, first put forward by Kraft, that the former is the anhydride of the latter.

In contradistinction to ergotinine, ergotoxine is strongly active physiologically, producing all the typical effects of ergot. It is contained in most commercial specimens of ergotinine, and also in Tanret's so-called "amorphous ergotinine."

DISCUSSION.

Dr. BYWATERS asked whether other alkaloids were known which passed from an inactive to an active form by being simply hydrated, and whether the fact of the active alkaloid being amorphous and forming a colloidal solution did not indicate that it was rather polymerisation instead of hydration that had occurred.

Dr. BARGER stated that some alkaloids were known which behave similarly to those mentioned in the paper. The salts of both alkaloids formed colloidal solutions under certain conditions.

*22. "*Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds.* Part VI. *The Partially Methylated* 4:6-*Diamino*-m-*xylenes.*" By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

In examining the effect of substitution on the formation of *o*-amino-azo-compounds of the benzene series, the authors have methylated progressively 4:6-diamino-*m*-xylene, and have studied the action of diazonium salts on the products. *Methyl*-4:6-*diamino*-m-*xylene* yields azo-derivatives like the unmethylated diamine itself, but as-*dimethyl*-4:6-*diamino*-m-*xylene* and *trimethyl*-4:6-*diamino*-m-*xylene* furnish stable diazoamines which are accompanied only by traces of azo-compounds.

DISCUSSION.

The PRESIDENT congratulated Dr. Morgan on the extreme ingenuity of the method by which he had effected the progressive methylation of these substituted *meta*-diamines. He asked with reference to the possible formation of aminoazo-compounds with the azo- and dimethyl-amino-groups in the *ortho*-position whether the action o

the usual transforming agents on the corresponding diazoamines had been tried, and if so with what result.

In reply to Dr. Cain's suggestion that steric hindrance might be the cause of the non-formation of azo-derivatives from tetramethyl-4 : 6-diamino-*m*-xylene, Dr. Morgan preferred to take the view that the absence of a labile hydrogen atom attached to nitrogen was the inhibiting factor. The non-formation of *ortho*azo-derivatives from tertiary amines was a general rule, which held both in the benzene and naphthalene series, whereas the phenomena attributed to steric hindrance in one of these series were frequently not manifested in the other.

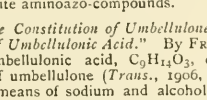
In reply to the President he stated that repeated attempts to transform the diazoamines of the *as*-dimethyl- and trimethyl-4 : 6-diamino-*m*-xylenes had not led to the isolation of definite aminoazo-compounds.

*23. "*The Constitution of Umbellulone.* Part II. *The Reduction of Umbellulonic Acid.*" By Frank Tutin.

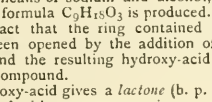
When umbellulonic acid, $C_9H_{14}O_3$, obtained by the oxidation of umbellulone (*Trans.*, 1906, lxxxix., 1104), is reduced by means of sodium and alcohol, a *hydroxy-acid* having the formula $C_9H_{18}O_3$ is produced. It is evident from this fact that the ring contained in umbellulonic acid has been opened by the addition of two atoms of hydrogen, and the resulting hydroxy-acid must therefore be a chain-compound.

This hydroxy-acid gives a *lactone* (b. p. 246—248°), and when oxidised with permanganate in presence of an excess of alkali yields acetic and *iso*propylsuccinic acids.

In the previous communication (*loc. cit.*) it was shown that umbellulonic acid must contain either a methylpentamethylene or a dimethyltetramethylene ring. Only two keto-acids containing either of these rings are capable of giving on reduction a hydroxy-acid, which, by subsequent oxidation, would yield acetic and *iso*propylsuccinic acids, namely, those possessing the following formulæ :—



I.



II.

A hydroxy-acid which would yield on oxidation acetic and *iso*propylsuccinic acids, could only be formed from one of the above keto-acids by the opening of the ring on reduction at the place indicated by the dotted line. The product of the reduction of umbellulonic acid will therefore be *δ-hydroxy-α-*iso*propyl-n-hexoic acid*,—

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH{\cdot}(CO_2H){\cdot}CH(CH_3)_2.$$

Formula II. represents pinononic acid, and it has previously been shown that umbellulonic acid is neither identical nor stereoisomeric with this compound. Umbellulonic acid must therefore be correctly represented by Formula I.

It follows from this that the correctness of the formula previously assigned to umbellulone cannot be doubted.

*24. "*The Reduction of Hydroxylaminodihydroumbelluloneoxime.*" By Frank Tutin.

Hydroxylaminodihydroumbelluloneoxime was prepared by Power and Lees in their investigation of the essential oil of *Umbellularia Californica* (*Trans.*, 1904, lxxxv., 636). When reduced with sodium and alcohol it gives a *base* (b. p. 136—138°/50 mm.), which is a liquid soluble in water. From the results obtained by the analysis of the *dibenzoate*, *dihydrochloride*, and *dibenzoyl* derivative of this base it is impossible to say with certainty whether it has the formula $C_{10}H_{20}N_2$ or $C_{10}H_{22}N_2$, although it is most probable that the latter is correct. The base may therefore be designated *aminotetrahydroumbellulylamine*.

Aminotetrahydroumbellulylamine dibenzoate crystallises in needles melting at 212—213° ; the *dihydrochloride* also forms needles, but it is infusible at 305°. *Dibenzoylaminotetrahydroumbellulylamine* crystallises in prisms or in leaflets, which melt at 194°.

Although evidence was obtained of the presence of bases which are probably stereoisomeric with aminotetrahydroumbellulylamine, no derivative of them could be isolated in a state of purity.

25. "*Studies on Optically Active Carbimides.* Part V. *The Aryl Esters and the Amides of l-Menthylcarbamic Acid.*" By Robert Howson Pickard and William Oswald Littlebury.

A continuation of the investigation of derivatives of menthylamine (see *Proc.*, 1905, xxi., 286). Eleven aryl esters and eighteen amides of *l*-menthylcarbamic acid were described, and the rotations of these when dissolved in chloroform and pyridine compared. Attention was drawn to the approximately constant molecular rotation given by certain derivatives of menthylamine and menthol.

26. "*Some Constituents of Natural Indigo.*" (Part I.). By Arthur George Perkin and William Popplewell Bloxam.

Indigo-brown, an impurity of natural indigo, is best isolated by means of boiling pyridine. The crude product contains, in addition to small quantities of indirubin and a colourless wax, certain brown amorphous substances, of which the compound (*a*), $C_{16}H_{12}O_3N_2$, is present in by far the largest amount. This substance is insoluble in all the usual solvents except pyridine, but dissolves in alkali hydroxide solutions, and is readily reduced in this condition. When digested with strong aqueous potassium hydroxide it is converted into anthranilic acid and an amorphous brown substance of uncertain composition. Two closely allied compounds (*b*) and (*c*) present in but small amount have been isolated, the former of which is soluble in acetic acid and insoluble in alcohol, whereas the latter dissolves in alcohol. These substances, to which the respective compositions $C_{24}H_{22}O_5N_3$ and $C_{16}H_{14}O_4N_2$ are ascribed, closely resemble in general properties the compound $C_{16}H_{12}O_3N_2$, and from them also anthranilic acid was obtained. It is considered possible that these brown compounds are derivatives or condensation products of indoxyl, which are formed from indican during the process of manufacture. The leaves of the *Indigofera arrecta* and *I. Sumatrana* are practically devoid of tannin matter.

27. "*The Occurrence of Isatin in some Samples of Java Indigo.*" By Arthur George Perkin.

During the examination of samples of Java indigo rich in indirubin, for yellow colouring matter (*Proc.*, 1904, xx., 172) by extraction with sodium carbonate solution and isolation of the products from the neutralised liquid with ether, there was obtained in addition to kampherol a small amount of substance crystallising from benzene in orange needles melting at 200°. This gave the thiophen reaction and was found to consist of isatin. The quantity present was exceedingly small, and in many other samples it appeared to be absent, but the point is interesting as it indicates that the formation of indirubin during the manufacture of natural indigo follows the well known synthesis of Baeyer (*Ber.*, 1881, xiv., 1745). Indirubin appears to be most readily formed when the fermented plant extract is oxidised under slightly alkaline conditions, and in these circumstances the oxidation of a portion of the indoxyl to isatin would appear to be facilitated.

28. "*The Absorption Spectra of Benzoic Acid, the Benzoates, and Benzamide.* By Walter Noel Hartley and Edgar Percy Hedley.

The absorption spectra of benzoic acid and phthalic acid were photographed by Hartley and Huntington, and characteristic bands were found in both; those of the

former being situated between λ 280 and λ 270 with a continuous absorption beyond λ 255.

In a paper by Baly and and Collie (*Trans.*, 1905, lxxxvii., 1332) it is stated that "The spectrum of benzoic acid has been observed by Hartley and Huntington (*Phil. Trans.*, 1879, clxx., I., 257) and only shows general absorption rather strongly. This is only to be expected from the presence of the ketonic oxygen in the β-position."

As many benzoyl derivatives show absorption bands in their spectra, including benzaldehyde, it was considered necessary to settle this question decisively.

The absorption curves of benzoic acid, potassium and silver benzoates, and benzamide have been drawn from the photographs of the spectra of these substances, which were specially prepared and were of great purity and finely crystallised. The absorption bands of the different substances are all obviously related to the bands in benzoic acid, and the absorption is due to the benzene ring.

29. "*The Absorption Spectra of Phthalic, Isophthalic, and Terephthalic Acids, Phthalic Anhydride, and Phthalimide.*" By Walter Noel Hartley and Edgar Percy Hedley.

Phthalic acid was examined by Hartley and Huntingdon (*Phil. Trans.*, 1879, clxx., I., 257), but the isomeric acids have not been investigated. The sparing solubility of terephthalic acid rendered it necessary for its examination to convert it into the dimethyl ester and to examine salts of the acid. It was found that phthalic anhydride, dissolved in cold alcohol, gave no absorption band, but that after warming for five minutes the spectrum showed a marked extension, and finally a strong absorption band was developed.

Phthalimide underwent no such change; it is therefore apparent that the group $\begin{matrix}CO\\CO\end{matrix}>NH$ is more stable than $\begin{matrix}CO\\CO\end{matrix}>O$.

o-Phthalic acid gives an absorption curve of the character that might be expected from a comparison with that of benzoic acid and from the difference in constitution between the two.

*iso*Phthalic acid has a shallow band of absorption situated in the same position as that of phthalic acid, but it is much less persistent.

Terephthalic acid being insoluble, its dimethyl ester and salts were examined, and it was found that the acid has no band, but merely an extension at or near where a band might be expected.

39. "*αα*γ-*Trimethyl- and αα*γγ-*Tetramethyl-Tricarballylic Acids and αδ-Dimethylbutane-*αβδ-*Tricarboxylic Acid.*" By Henry Henstock and Charles Henry Graham Sprankling."

In a former communication by Bone and Sprankling, a method was given for the preparation of alkyl tricarballylic acids in alcohol solution; in the case of the acids here discussed, the method has been modified and toluene was used instead of alcohol. The two reactions, (1) the condensation of the sodium compound of β-methylcyanosuccinic diethyl ester with α-bromo*iso*butyric ethyl ester, and (2) the condensation of the sodium compound of βδ-dimethylcyanosuccinic diethyl ester with α-bromopropionic ester, should both yield products from which, on hydrolysis, *αα*γ-trimethyltricarballylic acid should be obtained. It was found, however, that in reaction (1) *αδ*-dimethylbutane-αβδ-tricarboxylic acid is produced; probably hydrogen bromide is first eliminated from α-bromo*iso*butyric ester, and the resulting methylacrylic ester condenses with the sodium compound of β-methylcyanosuccinic ester as follows:—

$$CO_2Et\cdot CHMe\cdot CNa(CN)\cdot CO_2Et + CH_2{:}CMe\cdot CO_2Et = CO_2Et\cdot CHMe\cdot C(CN)(CO_2Et)\cdot CH_2\cdot CMeNa\cdot CO_2Et.$$

Reaction (2) yields *αα*γ-trimethyltricarballylic acid.

The condensation of *ββ*-dimethylsodiocyanosuccinic diethyl ester with α-bromo*iso*butyric ester furnishes a product which, on hydrolysis, yields *αα*γγ-tetramethyltricarballylic acid.

31. "*A Reaction of certain Colouring Matters of the Oxagine Series.*" By Jocelyn Field Thorpe.

Those colouring matters of the oxazine series which are derivatives of phenonaphthoxazine containing amino- or substituted amino-groups in the position 6 of the phenonaphthoxazine ring, are readily converted into the corresponding phenonaphthoxazone by warming on the water-bath in the presence of very dilute acids. Thus Nile-blue A (3-diethylamino-6-aminophenonaphthoxazine sulphate) and Nile-blue 2B (3-diethylamino-6-benzylaminophenonaphthoxazine chloride) are converted into 3-diethylaminoophenonaphthoxazone, melting at 204°, whereas New Methylene-blue GG (3 : 6-tetramethyldiaminophenonaphthoxazine chloride) and New Blue B (3-dimethylamino-6-dimethylaminophenylaminophenonaphthoxazine chloride) are converted into 3-dimethylaminophenonaphthoxazone, melting at 244°. Also those compounds which contain no substituting group in the position 6 in the phenonaphthoxazine molecule pass on warming with dilute acids into the corresponding oxazones containing the oxygen in that position. Thus, Meldola's blue (3-dimethylaminophenonaphthoxazine chloride) passes into 3-dimethylphenonaphthoxazone, melting at 244°, identical with the compound derived from New Methylene-blue GG and New Blue B.

32. "*The Alkylation of* d-*Fructose.*" By Thomas Purdie and David McLaren Paul.

The object of this research was to ascertain if ketoses can be alkylated by the methods already applied to aldoses, and to study the optical activity of the ketose derivatives thus obtained, Fischer's methylfructoside was methylated by means of methyl iodide and silver oxide. The resultant liquid, which had the composition of tetramethyl methylfructoside, gave on hydrolysis a liquid having the composition of tetramethyl fructose and the properties of a reducing sugar. On realkylation, both by the silver oxide process and by Fischer's method, the substance yielded fully methylated methylfructosides. The rotatory powers of the series of compounds were abnormally low compared with that of the parent sugar. This anomaly, however, was finally explained by the isolation from the syrupy ketose of crystalline tetramethyl-α-fructose (m. p. 98—99°), which showed in alcoholic solution $[\alpha]_D$ 20° − 94·2° ⇒ − 86·7°. After fusion, the substance exhibits mutarotation in the opposite sense, owing to partial transformation of the α-sugar into the β-form. This compound gave liquid tetramethyl methylfructosides of high rotatory power. Evidence was obtained that the low rotatory power of the syrupy ketose was probably due to the presence of an isomeric dextrorotatory hexose, produced by isomeric change during the preparation of Fischer's methylfructoside. Evidence was also adduced for the existence of two stereoisomeric fructosides in the latter substance.

(To be continued).

PHYSICAL SOCIETY.

Annual General Meeting, February 8th, 1907.

Prof. J. Perry, F.R.S., President, in the Chair.

Report of the Council.

Since the last annual general meeting twelve ordinary science meetings and one informal meeting of the society have been held. Of these, twelve were held at the Royal College of Science, and one, that on March 23rd, was held at University College. The average attendance at the meetings has been 50.

The second annual exhibition of apparatus by manufacturers was held on December 14th, when the attendance of Fellows and visitors amounted to 200.

The number of Fellows now on the roll is 426. Twelve new Fellows have been elected, and two Honorary Fellows, namely, Prof. F. Kohlrausch and Prof. A. A. Michelson. There have been 10 resignations, and the society has to mourn the loss by death of two Honorary Fellows, Prof. S. P. Langley and Prof. Ludwig Boltzmann, and two Fellows, namely, A. G. Bessemer, jun., and Prof. J. Purser.

The council are pleased to report that arrangements have been completed whereby Fellows now have the privilege of obtaining Section A of the Proceedings of the Royal Society at a reduced rate.

Report of the Treasurer for the Year 1906.

The difficulty of collecting arrears of subscriptions, alluded to in the report for 1905, has been severely felt during the past year. The arrears now stand at a higher figure than for some time past. Many correspondents attribute their inability to keep up to date to the long continued prevalence of a high income-tax, which hits many members of our society rather seriously. With this exception the position of the society is fairly prosperous. The value of the invested funds has not appreciably declined, the bank balance shows a substantial increase, and there are no outstanding liabilities.

Election of Officers and Council.

The following Officers and Council were elected for the ensuing year:—

President—Prof. J. Perry, F.R.S.

Vice-Presidents—Those who have filled the Office of President, together with C. Chree, D.Sc., F.R.S.; H. M. Elder, M.A.; Prof. J. A. Fleming, M.A., D.Sc., F.R.S.; and W. Watson, D.Sc., F.R.S.

Secretaries—W. R. Cooper, M.A., and Prof. W. Cassie, M.A.

Foreign Secretary—Prof. S. P. Thompson, D.Sc., F.R.S.

Treasurer—Prof. H. L. Callendar, M.A., F.R.S.

Librarian—W. Watson, D.Sc., F.R.S.

Other Members of Council—T. H. Blakesley, M.A.; A. Campbell, B.A.; W. Duddell; A. Griffiths, D.Sc.; J. A. Harker, D.Sc.; T. Mather, F.R.S.; A. Russell, M.A.; S. Skinner, M.A.; S. W. J. Smith, M.A.; Prof. H. A. Wilson, F.R.S.

Election of Honorary Fellows.

Prof. A. Lippmann and Prof. S. Newcomb were elected Honorary Fellows of the Society.

The President then delivered an address. He said that many present were aware that in August, 1905, he started a discussion at Johannesburg on the teaching of elementary mechanics. In his reply to that discussion he had tried to make clear his views about engineer's units and centrifugal force. It was time that the schoolmaster should recognise that engineers' units based on the weight of one pound in London were as absolute as any other units could possibly be, and when the schoolmaster rejected the term centrifugal force he merely showed that he had done no advance work in kinetics. Centrifugal force was natural and right to any boy, and if his schoolmaster did not teach him through the ideas that he had already, ideas which he found easy to understand, the schoolmaster was doing much worse than showing that he had learned his kinetics altogether from the astronomical side. It was the same with the pound as a unit of force. The ideas that quantity of matter was a simple thing to understand, that quantity of matter and inertia were the same and must be called *mass* were metaphysical, grown up, mixtures of abstractions which were quite unnatural and occult to young students whose experience had been with forces and weights. By simple experiments a young student should be given the fundamental idea that force is (vector) rate of change of momentum and his real knowledge of mathematics would increase greatly. The teaching of mathematics was a subject of enormous interest. Was it possible for any man who had been taught mathematics, and who knew nothing of recent reforms, to believe that the whole system on which he had been taught was quite wrong? Newspaper critics in reviewing his book containing the discussion to which he had referred, had ridiculed his standard boy of 14 who was in the future to know something of the infinitesimal calculus, and they had classed him with Macaulay's fabulous schoolboy. He was glad to say that this standard boy of 14 was a boy of the near future, and that there were some schools in which he was already being developed. It never seemed to occur to the orthodox mathematician that much of the work he tries to give the schoolboy was work that ought not to be touched by a man until after he was a wrangler. In Algebra alone a lot of unnecessary work was done on such subjects as anomalous forms, involution and evolution, surds, roots of a quadratic formation leaning to numerous tricky examples when the straightforward information required might be put in four lines. The same was true of the treatment of imaginary expressions, of ratio and proportion, of scales of notation, and of the progressions and continued fractions. Why was it that the subject of permutations and combinations must precede the binomial theorem? Simply to enable tricky questions to be asked on the binomial. If mathematical gymnastics were wanted they could be obtained in large quantity in the use of the calculus in its interesting applications. The classes in practical mathematics were showing that a board school boy after 50 lessons could use the idea of rate and could differentiate and integrate practically all the functions which were of use in engineering. A standard boy should know decimals at eight, he should use squared paper to record his own experimental results at nine, he should solve interesting problems using squared paper and logarithms and tables of sines and cosines at the age of ten and eleven, and he should get the notion of a rate long before he was twelve. He would have an elementary knowledge of the infinitesimal calculus before he was fourteen. He considered the elementary use of the calculus, and even the solution of easy differential equations, a school and not a university subject. Spherical harmonics and Bessel functions and their use in all sorts of physical problems with actual curve drawing was an undergraduate study. Permutations and combinations and the theory of probability were post-graduate subjects like the study of the fifth book of Euclid.

An Ordinary Meeting of the Society was then held.

Mr. A. Russell read a paper on "*The Magnetic Field and Inductance Coefficients of Circular, Cylindrical, and Helical Currents.*"

The author gives formulæ for the magnetic force near a circular current which can be readily evaluated. He then shows how the self-inductance of a ring of wire and the mutual inductance between two coaxial circular filaments can be found without using Neumann's theorem. By Kelvin's method, the results obtained can be applied at once to the corresponding problem of the simple vortex filament in hydrodynamics, In this way expressions are found for the velocity of translation of a circular vortex filament—about which there appears to be uncertainty in hydrodynamical theory—and for the energy of the motion. The exact formula for the mutual inductance between a cylindrical current sheet and a coaxial helical filament of current is obtained. It is expressed both in terms of elliptic integrals and in the form of an algebraical series. In the latter case it can be readily computed in important practical cases, as, for instance, in the case of the mutual inductance standards used to calibrate the galvanometers used in iron testing. The helical coils can be made of the same axial length and the pitch of only one of them need be small. Thus very compact standards can be constructed. It is shown that Lorenz's formula for self-inductance is a particular case of the author's formula for mutual inductance, and that a well-known formula due to Lord Rayleigh is a particular case of Lorenz's formula.

When the length of the helix is greater than twice its diameter and the pitch of the helix is small the self-inductance L is given by—

$$L = 2\pi(a^2/h)N^2[1 - 4a/3\pi h + a^2/8h^2 - a^4/64h^4];$$

where N is the number of turns, $2a$ the diameter, and $2h$ the axial length. The maximum inaccuracy of this formula, as compared with the more accurate elliptic integral formula, is less than 1 in 8000. The author has found this formula useful in practical work.

Mr. A. CAMPBELL said the accurate calculation of mutual inductances was of great practical importance because it formed the basis of several of the chief methods of determining the absolute electrical units: it was therefore highly satisfactory that Mr. Russell had succeeded in obtaining the complete solution for the most general case required. The author's series solution (41) was a most interesting one, When the length of one of the coils was very small compared with that of the other the series became practically o/o. This was the case used by Prof. Jones. Mr. Campbell suggested that from the author's series formula a suitable series might be obtained by differentiating with regard to h_2 (omitting the h_2 in the denominator). In calculating mutual inductance by Mr. Russell's complete formula (38) or by that of Prof. Viriamu Jones, it was necessary to find the incomplete integrals E (c, ϕ) and F (c, ϕ). These could often be found to a high degree of accuracy by the following two formulæ due to Legendre, viz.—

$$E(c, \phi) = \frac{1}{c}\sin c\phi + \frac{l^2c^2}{30}\phi^5 - \frac{l^2c^2}{1260}\phi^7(4 - 11c^2),$$

and—

$$F(c, \phi) = \frac{1}{c}\log_e\left(\frac{\pi}{4} + \frac{c\phi}{2}\right) - \frac{l^2c^2}{30}\phi^5 + \frac{l^2c^2}{1260}\phi^7(4 - 41c^2);$$

where $l^2 = 1 - c^2$. The first formula is accurate to 7 decimal places if $\phi < 30^\circ$ and the second to a similar accuracy if $\phi < 20^\circ$ or if ϕ 30° when $c <$ sin 35° or $>$ sin 75°.

Mr. A. RUSSELL in reply, after thanking Mr. Campbell for his remarks, called attention to the important relations between the equations of vorticity in hydrodynamics and the equations of electro-dynamics. He had experienced difficulty in conceiving the nature of the stress in the medium surrounding an electric current. Was the energy stored in the medium when a current was flowing kinetic or potential? Some physicists spoke as if the state of stress in the medium was due to streams of ether whirling round the electric current; others, that it was due to a compression of the medium.

NOTICES OF BOOKS.

Science and Agriculture in 1906. By Sir JAMES BLYTH, Bart.

THIS brief review has to chronicle many notable advances in the task of inducing the practical agriculturist to recognise the value of the applications of scientific methods to the problems he has to face, although there still remains much to be done in this direction. Some of the most important developments during the year 1906 include the discoveries made by the Agricultural Department of the University of Cambridge relating to the hybridisation and improvement of wheat, which has been the subject of research for some years past, although no very definite results have been obtained until quite recently. Important experiments have also been made at Rothamsted and other places on the use of artificial fertilisers, and the year has seen some valuable discoveries in connection with the prevention and cure of plant diseases. The pamphlet contains some suggestions which, if adopted, might extend the usefulness of the Board of Agriculture, and give a great impetus to the agricultural industry in England.

Painters' Colours, Oils, and Varnishes. By GEORGE H. HURST, F.C.S. Fourth Edition. London: Charles Griffin and Co., Ltd. 1906.

THE latest edition of this work contains, among other additions, descriptions of new processes for preparing white-lead which are now coming into use, and the chapter on lakes has been much enlarged. While the book is not a laboratory guide, the practice of the manufacture of paints and their analysis is fully treated, and the theory underlying the most familiar methods is carefully explained, so that the reader should easily acquire an intelligent grasp of the main principles involved. The book is one which can be thoroughly recommended for the use of technical students, and the fourth edition is an excellent example of an up-to-date practical treatise, in which all branches of the manufacture and assay of pigments, paint, vehicles, driers, and varnishes are discussed at considerable length.

Lehrbuch der Allgemeinen, Physikalischen, und Theoretischen Chemie. ("Text Book of General, Physical, and Theoretical Chemistry"). By F. W. KUSTER. Parts I.—IV. Heidelberg: Carl Winter, 1906.

THIS treatise on general chemistry forms part of the new edition of Gmelin and Kraut's "Text Book of Inorganic Chemistry," now being published. The author has endeavoured to present the subject as simply as possible, without sacrificing completeness, believing that most theoretical books are far too difficult, and make unnecessarily large demands upon the student's previous knowledge. He has certainly produced a very readable text-book, and one which is more especially suitable for those who are looking forward to a career connected with some technical branch of chemistry, or for botanists or doctors who require some knowledge of chemical theory for special purposes, but who are hampered by the insufficiency of their acquaintance with mathematics—for many a serious drawback in the study of physical chemistry. The amount of theoretical knowledge, without which even elementary students now find themselves ill-equipped, is rapidly and constantly increasing, and at present there is undoubtedly some difficulty in finding a suitable work. This the author of the present treatise seems likely to provide, judging from these first parts, which are clearly written, and contain a specially lucid treatment of some points, often found rather difficult to grasp, such as the Phase Rule.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 5, February 4, 1907.

The Ethyl Ether-oxide of α_1-Dichlorisopropylic Alcohol, and Dibromacetic Aldehyde.—P. Freundler.—In consequence of a recent publication of a research upon dichloracetic aldehyde and the $\alpha\alpha$-dichlorisopropyl alcohol, the author describes some experiments of the same order, carried out by him with the object of obtaining lactic aldehyde. 1. He found that condensation of dibromacetic aldehyde with methyl magnesium iodide gave rise to $\alpha\alpha$-dibromisopropyl alcohol, a far less stable body than the dichlor alcohol, partially decomposing on distillation. 2. Another body investigated was the ethyl ether-oxide of $\alpha\alpha$-dichlorisopropyl alcohol, $CH_3.CH(OC_2H_5).Cl_2$, which forms as an accessory product in the preparation of trichlorobutyric acetal. The attempt to transform it into

ethyl lactic aldehyde, by heating it in a closed vessel with lead oxide and water, did not succeed. 3. In the study of dibromacetic aldehyde are mentioned the reactions with phenyl hydrazine and semicarbazide, which produce corresponding derivatives of glyoxal.

Certain Reactions of Sodium Amide.—Louis Meunier and E. Desparmet.—To the already large collection of researches in organic chemistry, in connection with the use of sodium amide, the authors add the following:—1. The action of sodium amide upon certain polyhalogen derivatives of the carbides. 2. The use of sodium amide as a substitute for the ethylate in obtaining sodium derivatives. 3. The action of sodium amide upon the aldehydes. I. (*a*) The action of ethylene dibromide upon sodium amide produces acetylene,—

$$CH_2Br—CH_2Br+2NH_2Na=CH\equiv CH+2NaBr+2NH_3.$$

(*b*) The action of chloroform upon sodium amide—by dropping the latter in minute quantities in the powdered state into excess of chloroform to avoid explosion—produces sodium cyamide,—

$$CHCl_3+4NH_2Na=CNNa+3NaCl+3NH_3;$$

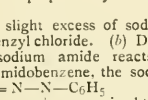
if the equation be written thus—

$$NH_2Na+CHCl_3+3NH_2Na=CNNa+3NaCl+3NH_3$$

it is seen to be identical with that which occurs in the preparation of the carbylamines,—

$$NH_2R+CHCl_3+3KOH=CNR+3KCl+3H_2O.$$

II. (*a*) As an example of the sodium derivatives of the primary and secondary amines, diphenylbenzylamine, $\begin{matrix}C_6H_5\\C_6H_5\\C_6H_5—CH_2\end{matrix}\!\!>\!N$, was prepared by adding diphenylamine, drop by drop, to a slight excess of sodium amide, in an ether solution of benzyl chloride. (*b*) Diazo-amide sodium derivatives. If sodium amide reacts with an ether solution of diazoamidobenzene, the sodium derivative of formula $C_6H_5—N=N—\underset{\displaystyle Na}{\underset{|}{N}}—C_6H_5$ is obtained. (*c*) Sodium derivatives of ethyl malonate. One molecule of sodium amide reacting with one molecule of ethyl malonate, in anhydrous benzene solution, produces in the cold a transparent gelatinous body, with the probable formula—



which, heated on the water-bath, evolves ammonia, and is converted into the liquid sodium derivative $CHNa<\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix}$, and this, when heated with one molecule of ethyl iodide, produces ethyl ethyl-malonate with precipitation of sodium iodide. III. When anhydrous ethyl aldehyde is allowed to fall drop by drop upon sodium amide, a white crystalline precipitate is obtained with evolution of ammonia. This can only be explained by the following equation:—

$$CH_3—COH+2NH_2Na=CH_3—CH=NNa+NaOH+NH_3.$$

The crystalline deposit probably consists of a mixture of aldehydate and imine of sodium.

MISCELLANEOUS.

Death of Henri Moissan.—We have just received information of the death of the eminent French chemist Henri Moissan, whose researches on the artificial production of diamonds and the electric furnace are familiar to our readers. We hope to give an obituary notice in our next issue.

Royal Institution.—On Thursday next, February 28th, at 3 o'clock, Dr. W. Martin begins a course of two lectures at the Royal Institution on "Old Dutch Paintings and Painters." The Friday Evening Discourse on March 1st will be delivered by Count de Bosdari on "Dante in the Critical and Poetical Works of Carducci," and on March 8th by Professor David James Hamilton on "Certain Seasonal Diseases in the Sheep and the Means of Preventing them."

South-Western Polytechnic, Chelsea.—The Lord Alverstone, G.C.M.G., Lord Chief Justice of England, presents Prizes and Certificates to Students of Evening Classes and Day College on March 15th, at 8 o'clock, p.m.

Merchant Venturers' Technical College.—There were 58 candidates for the post of Assistant Professor of Chemistry in the Merchant Venturers' Technical College, which has been vacated by Professor G. P. Darnell-Smith on his appointment as Assistant Director of Technical Education to the Board of Education, Auckland, New Zealand. Dr. F. W. Rixon has been selected from among these candidates. He had a distinguished career in the Victoria University of Manchester, which he entered with a Lancashire County Council Scholarship in 1896, and where he took the Degree of B.Sc. with First-class Honours in Chemistry in 1899, proceeding to the M.Sc. Degree in 1902. In 1900 he was elected to a Fellowship in the University, and in 1901 he was awarded an 1851 Exhibition Scholarship, which enabled him to continue his studies at the University of Giessen, where in 1903 he obtained his Ph.D. Degree. It will be seen that he has spent seven years as a University student of Chemistry and the allied Sciences; during the last four of these years he was engaged in original research work and published papers on questions dealing with various branches of Chemistry. Since 1903, Dr. Rixon has held the post of Science Instructor to the Devonshire County Council.

MEETINGS FOR THE WEEK.

Monday, 25th.—Society of Arts, 8. (Cantor Lectures). "Romanesque Ornament," by F. Hamilton Jackson.

Tuesday, 26th.—Royal Institution, 3. "The Visual Apparatus of Man and Animals," by Prof. William Stirling.

Wednesday, 27th.—Society of Arts, 8. "Modern Typewriters and Accessories," by Arthur E. Morton.

Thursday, 28th.—Royal Institution, 3. "Old Dutch Painting and Painters," by Dr. W. Martin.

Friday, March 1st.—Royal Institution, 9. "Dante in the Critical and Poetical Works of Carducci," by Count de Bosdari.

Saturday, 2nd.—Royal Institution, 3. "Röntgen, Cathode, and Positive Rays," by Prof. J. J. Thomson.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2466.

ON A NEW IRON CARBONYL, AND ON THE ACTION OF LIGHT AND OF HEAT ON THE IRON CARBONYLS.*

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S., Jacksonian Professor in the University of Cambridge, and HUMPHREY OWEN JONES, M.A., D.Sc., Fellow of Clare College, and Jacksonian Demonstrator in the University of Cambridge.

This paper contains an account of the results of the continuation of the experiments on the action of light on the liquid iron carbonyl (iron pentacarbonyl) and the action of heat on the resulting solid compound, diferro-nonacarbonyl, $Fe_2(CO)_9$, which were described in a paper on "The Physical and Chemical Properties of Iron Carbonyl," communicated to the Royal Society in 1905 (*Proc. Roy. Soc.*, A. 1905, lxxvi., p. 558).

The experiments on the action of light on iron pentacarbonyl under varied conditions have resulted in new and interesting observations, and approximate measurements of the velocity of the reaction induced by light have been made and compared with that of other reactions induced by light.

The action of heat on solid iron carbonyl, which we described in our former communication as producing an intense green colour, which colour Dr. Mond stated that he had observed casually, has been further examined, and the experiments now described have led to the discovery of a new compound of iron and carbon monoxide, iron tetracarbonyl, which forms dark green crystals of remarkable stability, exhibiting some very striking properties.

Action of Light on Iron Pentacarbonyl.

It was shown in the former communication that the action of light on iron pentacarbonyl alone or in solution in solvents, with the exception of nickel carbonyl, is represented by the equation $2Fe(CO)_5 = Fe_2(CO)_9 + CO$.

Carbon monoxide is evolved and diferro-nonacarbonyl, an orange-red crystalline compound, is produced and separates out. When pyridine was used as solvent, the diferro-nonacarbonyl remained in the deep red solution unless very much iron pentacarbonyl had been used, when some crystals were deposited.

The fact that solid is not deposited from a pyridin solution of iron pentacarbonyl under the action of light is attributed to the solubility of the diferro-nonacarbonyl in pyridine, since it was shown that solid was deposited when the solution contained more than 50 per cent of the pentacarbonyl (*loc. cit.*, p. 575). This has been confirmed by using a saturated solution of the diferro-nonacarbonyl in pyridine as solvent for the pentacarbonyl. A 20 per cent solution of iron pentacarbonyl in this mixture, on exposure to light for a long time deposited crystals. Owing to the deep colour of the solution, the action is naturally a very slow one. A 20 per cent solution of iron pentacarbonyl in pyridine alone would not have deposited any of the solid.

When nickel carbonyl was used as solvent no change occurred; the solutions were of a much paler colour than solutions of the same concentration in other solvents, and it was suggested that the two carbonyls united to form an unstable compound $\{Fe(CO)_5Ni(CO)_4\}$ which was analogous to $Fe_2(CO)_9$ and was unaffected by light.

Also it was shown that above 60° C. light had no apparent action on solutions of iron pentacarbonyl, and that the reaction induced by light was reversed in the dark.

The later experiments were directed towards confirming and extending the above observations.

Action of Light on Iron Pentacarbonyl at Higher Temperatures.

In the former communication (p. 574) it was stated that if iron pentacarbonyl or its solutions in ether or petroleum ether were heated to any temperature between 60° and 100° C. while exposed to light, then no separation of solid occurred, even after long exposure and subsequent cooling in the dark.

This remarkable behaviour has been further confirmed by exposing tubes to light while immersed in the vapours of various liquids and observing whether solid was deposited or not, while hot or after cooling in the dark, and also by using tubes provided with a manometer of the type used for the velocity measurements described below. Usually, petroleum ether solutions, containing about 10 per cent by volume of iron pentacarbonyl, were used; ether solutions were also used.

In ether vapour, 30° to 35° C., solid is slowly deposited, and the manometer shows an increase of pressure. On bright days, an appreciable amount of solid had formed after five minutes.

In the vapour of petroleum ether, 45° to 50° C., the solid was more slowly formed, but in half-an-hour on the same day a distinct amount of crystalline deposit had formed, and the manometer again indicated an increase of pressure.

In acetone vapour, 56° C., no solid was deposited after exposure for five hours to bright sunlight, no increase of pressure was noticed, and no solid was deposited when the tube was allowed to cool in the dark.

In chloroform vapour, 61° C., no change was observed after six hours' exposure to bright sunlight, no solid separated when the tube was cooled in the dark, and the manometer showed that no increase of pressure had occurred.

That the deposition of solid is a delicate and trustworthy indication of any change is proved by the fact that whenever any solid could be observed the manometer indicated an increase of pressure. The solid is extremely sparingly soluble in the two solvents, petroleum ether and ether, and so is deposited as soon as formed. Further, above 46° C., the solid is gradually decomposed, as will be described later, producing a green solution; no trace of this colour was ever observed in the tubes exposed to light at any temperature between 50° and 100° C., provided they contained no solid before they were heated. An experiment was made in which a solution of iron pentacarbonyl containing a little of the solid diferro-nonacarbonyl was heated to 56° C. and then exposed to light. A green colour was produced, but no solid was deposited after several hours.

It is noteworthy that neither on bright days in December nor in July could we observe any decomposition at temperatures about 56° C.; that is, no definite shifting of the transition temperature due to the difference in the intensity of the light could be observed.

These experiments will be discussed later, when the experiments on the reverse reaction have been described.

Approximate measurements of the velocity of the reaction were made in solutions in petroleum ether and in pyridine at two concentrations, and the rate in the two solvents compared. Since no artificial light had been found to effect the change at all rapidly, it was necessary to depend on sunlight, the intensity of which naturally varied considerably. Tubes of the same size were made to hold the solutions, and these were filled with solutions of arbitrary concentrations which were in the ratio of 2 to 1, so that information as to the "order" of the reaction might be obtained. These tubes were sealed on to a capillary tube, closed at the other end and containing a small pellet of mercury; measurements of the movement of this mercury index enabled us to determine the pressure inside the tubes. The tubes were set side by side in a glass tank of water, and exposed to direct sunlight and

* A Paper read before the Royal Society, January 24, 1907.

examined at intervals until no further change took place. Calculation of the fraction of the whole decomposed x/a, where a represents the final increase of pressure and is a measure of the initial concentration of the iron carbonyl, and x is the increase of pressure at any time and is a measure of the amount of decomposition that has taken place, shows clearly that the reaction proceeds as one of the "first order," since it will be seen that the fraction for each concentration is the same within as narrow limits as could be expected in the circumstances. The agreement is naturally not good at the beginning, since the solution must became saturated with the gas. It is probable that great supersaturation is prevented in the case of petroleum ether by the separation of solid; but in the case of pyridine, where no solid separates, this disturbing effect, which tends to make x/a too small at the beginning, is much greater, and good agreement is only obtained near the end of the reaction.

Another fact must also be taken into consideration as affecting the result: in the case of petroleum ether more solid separates from the more concentrated solution than from the other; in the case of pyridine it acquires a deeper colour, so that in both cases less light penetrates the more concentrated solution; in both cases, therefore, the amount of change is relatively less in the more concentrated solution towards the end. This is shown by the greater values of x/a for the dilute solution near the end.

The following two sets of experiments are sufficient to indicate the kind of result obtained:—

I.—*Solvent: Petroleum Ether.*

Time.	A. Concentration 2.		B. Concentration 1.	
	Pressure. Atmos.	x/a.	Pressure. Atmos.	x/a.
2 mins.	1·01	0·001	1·02	0·004
12 ,,	1·30	0·033	1·07	0·014
22 ,,	1·72	0·079	1·30	0·060
32 ,,	2·25	0·147	1·47	0·094
42 ,,	2·46	0·16	1·81	0·16
55 ,,	2·70	0·19	2·05	0·21
112 ,,	3·86	0·32	2·69	0·34
142 ,,	4·26	0·36	2·80	0·36
182 ,,	4·76	0·41	3·25	0·45
247 ,,	5·40	0·47	3·55	0·51
28 hours	7·36	0·70	4·33	0·67
2 days	8·1	0·78	5·2	0·84
∞	10·1	1·0	6·0	1·0

II.—*Solvent:* C *and* D, *Pyridine;* E, *Petroleum Ether.*

Time.	C. Conc. 2.		D. Conc. 1.		E. Conc. 2.	
	Pressure. Atmos.	x/a.	Pressure. Atmos.	x/a.	Pressure. Atmos.	x/a.
5 mins.	1·00	—	1·00	—	1·03	0·014
7 ,,	1·00	—	1·00	—	1·10	0·014
10 ,,	1·03	—	1·01	—	1·17	0·023
20 ,,	1·13	—	1·02	—	1·25	0·034
30 ,,	1·16	—	1·03	—	1·47	0·064
50 ,,	1·31	—	1·06	—	1·92	0·126
70 ,,	1·49	—	1·12	—	2·80	0·24
85 ,,	1·60	—	1·24	—	3·02	0·27
105 ,,	1·67	0·13	1·33	0·093	3·13	0·28
135 ,,	1·81	0·15	1·46	0·13	3·57	0·35
175 ,,	2·47	0·28	2·21	0·34	4·41	0·47
255 ,,	3·18	0·43	2·43	0·40	5·00	0·55
325 ,,	3·35	0·46	2·70	0·48	5·30	0·58
26 hours	4·78	0·76	3·47	0·70	5·78	0·65
52 ,,	5·12	0·81	4·07	0·86	6·83	0·80
∞	6·09	1·00	4·56	1·00	8·35	1·00

A tube set up in precisely the same way with nickel carbonyl as solvent showed during several months' exposure only very slight changes of pressure, which were due to temperature changes.

In order to compare the decomposition of iron carbonyl with other reactions induced by light, we compared the rate of evolution of gas from a solution of iron pentacarbonyl in petroleum ether with that from a solution of ferric chloride and oxalic acid. The latter action, which has been examined by Lemoine (*Ann. de Chimie et de Phys.*, 1895, [7], vi., p. 433), proceeds according to the equation $2FeCl_3 + H_2C_2O_4 = 2FeCl_2 + 2HCl + 2CO_2$, is exothermic, and at the ordinary temperature only takes place under the influence of light.

For the purpose of the approximate comparison, equimolecular solutions of iron pentacarbonyl in petroleum ether and of ferric chloride were used. In order to make the latter reaction approximate more nearly to a reaction of the "first order," two molecular proportions of oxalic acid were used (more cannot be added, since the solution then changes its colour and ferrous oxalate is deposited during the later stages).

Both solutions are yellow, but the colour of ferric salt solution is much deeper than that of the iron carbonyl at the same molecular concentration; hence the comparison is not quite fair, since the amount of change is proportional to the light absorbed, and the latter solution absorbs more light.

Two solutions were used, containing respectively 4 per cent and 10 per cent of iron carbonyl, and the rate of change compared with two ferric chloride and oxalic acid solutions of corresponding equimolecular concentrations.

The solutions were placed in tubes of the same size, which were placed side by side in a tank of water, and the gases evolved were collected over glycerin.

The volume of gas evolved from the ferric salt solutions is twice that evolved from the corresponding iron carbonyl solutions.

The ferric salt solutions were saturated with carbon dioxide before being introduced into the tubes, yet it is probable that the supersaturation of the solution which is set up causes a lag in the evolution of gas at the beginning. Later, the deposition of solid from the iron carbonyl solutions cuts off some of the light and further diminishes the rate of this action as compared with the other.

The results of six sets of experiments show that there is no very pronounced difference in the sensibility to light of the two reactions in the more concentrated solutions, but that in the more dilute solutions the ferric chloride and oxalic acid mixture is the more sensitive.

The following table gives the fractions of the total amount of gas evolved from the solutions during the same time:—

$Fe(CO)_5$, 10 per cent.	Fe_2, 2·86 per cent. $H_2C_2O_4$, 4·6 per cent.	$Fe(CO)_5$, 4 per cent.	Fe_2, 1·12 per cent. $H_2C_2O_4$, 2·86 per cent.
0·24	0·19	0·12	0·28
0·28	0·25	0·26	0·40
0·31	0·37	0·40	0·67
0·40	0·55	0·65	0·85
0·66	0·75	0·75	0·95
0·71	0·79		
0·82	0·94		

The figures for the dilute solutions do not represent readings taken at the same time as those for the more concentrated solutions.

From the above numbers no very definite conclusions can be drawn, but it is probable that iron carbonyl is more sensitive to light than the ferric chloride oxalic mixture, seeing that the decomposition is nearly as rapid in the former case as in the latter, and the amount of light absorbed by the ferric chloride and oxalic acid mixture is greater than that absorbed by the iron carbonyl solutions.

A rough comparison of the velocity of the decomposition of iron carbonyl with that of the reaction between mercuric chloride and oxalic acid, which was measured by the development of pressure due to the carbon dioxide, showed that the former reaction proceeded very much more rapidly than the latter under the same conditions.

Reversal of the Reaction.

The velocity of the reverse reaction,—

$$Fe_2(CO)_9 + CO = 2Fe(CO_5),$$

which proceeds in the dark, was studied by using the same tubes that were used for the examination of the direct action. The results show that this is an extremely slow reaction at the ordinary temperature. Tube E, above, containing petroleum ether, had a pressure of 3 atmospheres after three months, so that only 73 per cent of the gas had been re-absorbed by the solid; after eleven months the pressure was still 1·68 atmospheres, so that 92 per cent of the products had re-combined.

With pyridine as solvent the reverse action was more rapid at the beginning, but did not proceed so far. Thus, after fifteen days in the dark, tube D, containing pyridine, had a pressure of 1·8 atmospheres, representing 51 per cent recombination, while in the petroleum ether tube E only 28 per cent recombination had occurred at the same time.

The two tubes, A and B, containing petroleum ether, were used for studying the rate of the reverse reaction at higher temperatures. B was heated in ether vapour. In two days the pressure fell from 6 to 4·1 atmospheres, in five days to 2·8 atmospheres, in ten days to 1·6 atmospheres, and after sixteen days the reversal was complete, the solid had disappeared, and the pressure had fallen to 1 atmosphere. Similar results were obtained with other tubes. Attempts were made to study the reverse reaction at higher temperatures; in carbon disulphide vapour (46° C.) the reaction appeared to proceed more rapidly, but development of a green colour showed that already the decomposition of the diferro-nonacarbonyl by heat was beginning, and this naturally vitiated the results.

Results of precisely the same kind were obtained with methylal as solvent. The solid diferro-nonacarbonyl is slightly soluble in the solvent, and on heating gives a red solution—it is therefore intermediate in its behaviour between petroleum ether and pyridine; as in the case of pyridine the reverse action is also more rapid in the early stages than it is in ether or petroleum ether.

These observations on the greatly increased velocity of the reaction between diferro-nonacarbonyl and carbon monoxide at temperatures little above the ordinary temperature are of great importance in their bearing on the absence of any action of light on iron pentacarbonyl above 56° C.

Iron carbonyl shows no selective absorption, but completely absorbs the more refrangible rays.

It was found by spectroscopic examination of iron carbonyl and its solutions that there was no observable difference in the amount of light absorbed at 15° C., and at 60° or 100° C.

The absence of action of light above 56° C. must be due, therefore, either to a greater stability of the iron pentacarbonyl molecule at higher temperatures or to the displacement of an equilibrium represented by the equation $2Fe(CO)_5 \rightleftarrows Fe_2(CO)_9 + CO$, in the direction of the liquid carbonyl at the higher temperatures. The fact that the action of carbon monoxide on the diferro-nonacarbonyl is so much accelerated by an increase of temperature makes it probable that this is the true explanation. Lemoine (*loc. cit.*) has shown that the reaction between ferric chloride and oxalic acid exhibits no appreciable acceleration due to increase of temperature; the action of light on the silver halides is also little affected by temperature. If the decomposition of iron pentacarbonyl also has no temperature coefficient, which is not improbable, since we were able to observe the action at −180° C., and the reverse action has the normal temperature coefficient of chemical reactions, then the absence of any change at temperatures above 56° C. is easily explained.

This explanation is compatible with the assumption that the decomposition of the pentacarbonyl by light is an exothermic change, so that the reverse reaction must take place with absorption of heat, and an increase of temperature would favour the progress of the endothermic change, *i.e.*, the recombination of carbon monoxide and the diferro-nonacarbonyl.

We are continuing the experiments on these and other chemical reactions induced by light, and applying other methods in studying them, the results of which we hope to describe later.

(To be continued).

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 90.

Part I.—Preparation of the Solution.

General Discussion.

The attempt has been made to devise a systematic method of preparing the solution of the substance for analysis, which shall be uniform for all substances, which in the case of those ordinarily met with shall be as rapid as possible, and which shall be so complete as to effect the solution of substantially all known substances. Heretofore little attention has been given to the development of such a definite, uniform plan of treatment, it being assumed that the analyst has the experience necessary to enable him to select, on the basis of the known general character of the substance or of a series of preliminary tests in the dry way, the most suitable method to employ for its decomposition. Yet more experience is required for this than for the ordinary group separations; and there seems to be no reason whatever why this important and difficult part of the analytical process should not be treated in the same systematic way as are the separations and tests for the various elements.

The general character of the plan here presented for accomplishing this end will be readily seen from the "Tabular Outline" given below. The only preliminary test required is one for the presence of organic matter and water, which is made by heating the substance in a closed tube; thus are eliminated the time-consuming blowpipe tests usually recommended, the success of which can be assured and the true significance interpreted only after much experience. For substances found to contain organic matter a special treatment with nitric and sulphuric acids is described by which the organic matter is destroyed. Other substances are treated first with water, and, if this does not cause complete solution, immediately after with fairly strong nitric acid; and any residue still remaining is boiled with hydrochloric acid and aqua regia, in order to remove a few substances, such as manganese and lead peroxides, mercuric sulphide, gold, and platinum, which are attacked by these acids, but not by nitric acid.

In the treatment of the residue that may remain unattacked by these acids lies the main difference between our process and that ordinarily recommended in text-books on qualitative analysis; for, as shown in Table II., any such residue is heated with sulphuric and hydrofluoric acids instead of being fused with an alkaline carbonate. By this modification the process of preparing the solution is much simplified in the great majority of cases; for silica is thereby detected and eliminated at the start, and almost all silicates are decomposed, yielding at once either a complete solution, or, if lead, barium, strontium, or much calcium is still present, a residue of their sulphates which can readily be decomposed by boiling with sodium carbonate solution. An even more important advantage of this method, however, is that no foreign metallic elements are introduced; while, when a fusion is made, alkali

* From the *Technology Quarterly*, xix., No. 3, September, 1906.

TABLE I.

Determine by preliminary tests whether the substance contains organic matter (P. 1); and, if not, whether it dissolves completely in water and forms an acid or neutral solution (P. 3).

Substances containing Organic Matter.—Heat with H_2SO_4 and HNO_3 to destroy organic matter, evaporate off HNO_3, add water (P. 2).

Residue. See Table II. or III. below.

Solution.—Add HCl (P. 2).

Precipitate. AgCl. Confirm by P. 15.

Filtrate. All elements except Ag, Cr, Pb, Ba, Sr. Pass in H_2S (P. 21).

Substances Soluble in Water forming a Neutral or Acid Solution.—Dissolve in water, add HCl (P. 11).

Precipitate. AgCl, HgCl, [$PbCl_2$], [TlCl]. (P. 12).

Filtrate. All elements except Ag. Pass in H_2S (P. 21).

Other Substances.—Heat with HNO_3, evaporate, dry, add dilute HNO_3 (P. 3).

Solution.—Add HCl (P. 3).

Precipitate. AgCl, [$PbCl_2$], [TlCl] (P. 12).

Filtrate. Evaporate; add HCl (P. 4).

Residue.—**A** (from alloys.—Sb_2O_5, SnO_2, [P_2O_5], [As_2O_5], SiO_2, [TiO_2], WO_3, C, Au, Pt, Ir, &c.; some iron alloys.

B (from other substances).—Oxides under **A** above and substances under **B** in Table II.; also MnO_2, PbO_2, and HgS.

Heat with HCl and HCl + HNO_3, evaporate, dry, add dilute HCl (P. 4).

Solution.—All elements except Ag. Pass in H_2S (P. 21).

Residue.—See Table II. or III. below.

TABLE II.

Residue Undissolved by Acids from Table I.

A. *From Alloys.*—[SnO_2], SiO_2, TiO_2, WO_3. (C, Ir, &c., some Fe alloys). NOTE.—A *metallic* residue obtained from an alloy is not treated as described in the table, but is best fused with Na_2O_2 (P. 4, N. 2).

B. *From Non-metallic Substances.*—Oxides under **A**; also AgCl, CaF_2, MoS_2, many silicates, the sulphates of Pb, Ba, Sr, native Al_2O_3, $FeO.Cr_2O_3$.

C. *From Substances containing Organic Matter.*—Substances under **B** (except CaF_2); also Sb_2O_5, $BiOSO_4$, $Cr_2(SO_4)_3$, $CaSO_4$.

Heat with H_2SO_4 and HF, evaporate to expel HF, dilute, boil (P. 5).

Gas. SiF_4. Presence of silicon.

Solution. All elements except Pb, Ba, Sr. Pass in H_2S (P. 21).

Residue.—Pb, Ba, Sr, [Ca,], [Bi], [Cr], as sulphates; Sb_2O_5, WO_3; native SnO_2, Al_2O_3, TiO_2, $FeO.Cr_2O_3$; some silicates. Boil with Na_2CO_3 solution (P. 6).

Solution. Na_2WO_4. Test for tungsten (*P. 6a).

Residue.—Pb, Bi, [Ba], Sr, Ca, as carbonate; [$BaSO_4$], other substances, except WO_3, as above. Heat with HCl (P. 6).

Solution. Pb, Bi, Sb, Cr, [Ba], Sr, Ca, as chlorides. Pass in H_2S (P. 21).

Residue.—[$Cr_2(SO_4)_3$], [$BaSO_4$], MoS_2, native oxides and silicates as above. Fuse with Na_2CO_3 and KNO_3, add HCl, evaporate, add dilute HCl (P. 7).

Solution. Test for all elements except alkalis (P. 21).

Residue.—SiO_2; native SnO_2, TiO_2, Al_2O_3. Remove SiO_2 with HF; fuse residue with KOH (P. 7, N. 3).

TABLE III.
(Alternative Process).

Residue Undissolved by Acids from Table I.

Composition: See Heading of Table II.

Fuse with Na_2CO_3 and K_2CO_3 in a porcelain crucible, adding KNO_3 if necessary; add water, filter (P. 8).

Solution.—Sodium and potassium silicate, stannate, antimonate, arsenate, aluminate, chromate, manganate, tungstate, molybdate, sulphate, and carbonate. Acidify, evaporate, dry, add dilute HCl (P. 8).	*Residue.*—Almost any metallic element as metal, oxide or carbonate. Add HNO_3 (P. 8).	
	Solution.—Almost any element as nitrate. Add HCl (P. 8).	*Residue.*—Native SnO_2, TiO_2, Al_2O_3. Fuse with KOH, add water and HCl (P. 7, N. 3), test solution for Sn, Al, Ti.
Solution.—Sn. Sb, As, Mo, Al, Cr, as chlorides. Pass in H_2S (P. 21).	*Residue.*—SiO_2, WO_3. Reject, or treat by P. 5 and *6a.	*Filtrate.*—Evaporate, add HCl, test for all elements except alkalis (P. 21). *Precipitate.*—AgCl, [$PbCl_2$] (P. 12).

elements are introduced from the flux, and aluminium, calcium, and silica from the porcelain crucible, which ordinarily must be used, owing to the possible presence of reducible metallic elements, thus making it necessary to employ other special methods for the detection of these elements. Objection may be raised to the use of hydrofluoric acid because of its being an expensive and irritating reagent, and because it must be handled in platinum vessels, thus making it hardly practicable for the use of large classes of beginners in the subject. Realising the force of the last consideration, we have described (as indicated in Table III.) the usual method of fusion with an alkaline carbonate as an alternative procedure, which may be used under circumstances which do not permit of the simpler and more satisfactory method with hydrofluoric acid. But in doing so we wish to express the conviction that when the subject of qualitative analysis is studied as a branch of analytical chemistry, and not merely as a means of imparting a certain additional chemical knowledge, it ought to be pursued under the same conditions with respect to accuracy of manipulation and availability of facilities as is customary in courses upon quantitative analysis. For the inability to make a good qualitative analysis is a common source of error in quantitative analytical results; and lack of thoroughness in the instruction in qualitative analysis often develops careless and inaccurate habits of work. We have therefore aimed to develop the scheme of analysis best adapted to the purposes of the analyst, and have not hesitated to avail ourselves of the special methods and reagents commonly used only in quantitative work when a more reliable or simpler process could thereby be developed.

Only few substances, especially a few silicates and native oxides, fail to be dissolved by the treatment with sulphuric and hydrofluoric acids; and it is very rare that any further operations are necessary. But to provide for these special cases it is directed to fuse any residue with alkaline carbonate and nitrate, which can now safely be done in a platinum crucible; and, finally, to fuse any residue still remaining (which is likely to consist only of aluminium, tin, or titanium oxide) with potassium hydroxide.

Tabular Outline.

In the "Tabular Outlines" the enclosure of a symbol in brackets shows that the element may divide itself between the residue and solution in the operation immediately preceding. The symbols of the anhydrous substances are given, without reference to the actual state of their hydration in the residue or precipitate.

(To be continued).

A DEDUCTION FROM WAALS'S EQUATION.

By R. H. McCREA.

IT has been stated that this equation gives no explanation of solidification, but a closer investigation of this point may be profitable.

In a solid, the constituent molecules, although free to vibrate, are taken as not free to wander as in the case of a liquid or gas. In other words, the intermolecular spaces, whatever be the ultimate nature of the molecules, have been in the case of the solid for the most part eliminated.

Writing the usual equation—

$$(v - b)(p + a/v^2) = K$$

in the form—

$$v - b = \frac{K}{p(1 + a/pv^2)}$$

let a mass of gas be compressed along an isothermal for a temperature above the critical. An increase of pressure in this direction will not produce liquefaction. There probably exists, also, a critical temperature for the solid state. Now, suppose the gas to be compressed along an isothermal above this to a point above the corresponding critical pressure, and then cooled so that its volume remains constant, where this line cuts the critical isothermal the substance will pass into the solid state.

Of course, the above is merely to clear the way for the following piece of extrapolation:—

The curve for the equation approaches to a rectangular hyperbola, and since the line representing the contraction of a solid under pressure is virtually a straight line parallel to the ordinate, and hence in this case to an asymptote of the curve; and as it is known that such a line meets the curve in one point at infinity, hence at an infinite distance along the pressure axis, that is, when the pressure is made infinite, the solid condition is reached.

Now, in the equation, let—

$$p = \infty.$$

Hence the right-hand side of the equation will be diminished infinitely; that is,—

$$v - b = 0.$$

This will happen if $v = b$ for any finite values, or if v and b each $= 0$. Taking the former as the elimination of the intermolecular spaces, and therefore as the attainment of the solid state, we see that the physical interpretation of the previous paragraph is in accordance with this mathematical development.

Now, returning again to the right-hand side,—

$$\frac{K}{p + a/v^2},$$

substitute b for v and we get the term a/b^2. In the case of carbon dioxide $a = 0{\cdot}00874$ and $b = 0{\cdot}0023$; hence—

$$\frac{a}{b^2} = \frac{0{\cdot}00874}{(0{\cdot}0023)^2} = 1652 \text{ atmospheres.}$$

In this case, also, R in the constant has a very small value,—

$$\frac{1{\cdot}00642}{273}.$$

Hence, neglecting p for the present, we see that—

$$\frac{RT}{a/b^2}$$

may have a very small value, approaching practically zero

When the solid state, then, has once been reached the great tension of the molecules, a/v^2, coupled with a low temperature, T, is sufficient to keep the expression $v - b = 0$ practically true, neglecting p; that is, as long as the temperature is kept low a solid may be kept as such through the tension of its molecules, even when the pressure has been greatly reduced.

There are conscious weaknesses in the above chain of reasoning, but it is hoped that it may not be altogether unsuggestive.

A REVISON OF THE ATOMIC WEIGHT OF MANGANESE.*

By GREGORY PAUL BAXTER and MURRAY ARNOLD HINES.

The following table, taken from Clarke's "A Re-calculation of the Atomic Weights" (Smith, Misc. Coll., "Constants of Nature," 1897, Part V., p. 283), gives a brief *résumé* of previous work upon the atomic weight of manganese which has other than historical interest.

O = 16·000.

Berzelius (*Ann. Physik. Chem.*, 1830, xviii., 74)—
$MnCl_2 : 2AgCl$ .. .. 55·12

Turner (*Trans. Roy. Soc. Edinb.*, 1831, xi., 143)—
$MnCl_2 : 2AgCl$ .. .. 54·92

Dumas (*Ann. Chem. Pharm.*, 1860, cxiii., 25)—
$MnCl_2 : 2Ag$.. .. .. 54·98

Von Hauer (*Journ. Prakt. Chem.*, 1857, lxxii., 360)—
$MnSO_4 : MnS$ .. .. 54·91

Schneider (*Ann. Physik. Chem.*, 1859, cvii., 605)—
$Mn : 2CO_2$ .. .. 54·03

Rawack (*Ibid.*)—
$Mn_3O_4 : H_2O$ .. .. 54·08

Dewar and Scott (*Proc. Roy. Soc.*, 1883, xxxv., 44)—
$AgMnO_4 : AgMnO$ .. .. 54·86
$AgMnO_4 : 2KBr$ .. .. 55·02

Marignac (*Arch. Sci. Phys. Nat.*, 1883, [3], x., 21)—
$MnO : MnSO_4$ .. .. 55·01

Weeren, (Dissertation, Halle, 1890)—
$MnO : MnSO_4$ .. .. 55·00
$MnS : MnSO_4$ .. .. 55·00

From these results Clarke computes the most probable value to be 54·987.

The close agreement of the greater part of these determinations is striking, the experiments of Schneider and Rawack being the only ones which indicate a value for manganese very different from 55·0. The variations of their results from the others is not surprising, however, since manganoso-manganic oxide and manganous oxalate, with which they worked, are undoubtedly difficult to obtain in a pure condition. The remaining determinations all fall within limits 0·26 of a unit apart, and all but two agree within 0·16 of a unit. Our present knowledge concerning the variety of atomic weights upon which the above determinations are based is not sufficiently certain to lead to the expectation of closer agreement from such widely different methods. (Richards and Wells, "Publications of the Carnegie Institution," No. 28, 1905, p. 67; "Report of the International Committee on Atomic Weights," *Journ. Am. Chem. Soc.*, 1906, xxviii., 6).

For this investigation the substances chosen for examination were manganous chloride and bromide, since the analysis of halogen compounds may be effected with great accuracy. Furthermore, these compounds have not been investigated by any of the more recent experimenters except Dewar and Scott (*loc. cit.*), who performed one analysis each of the chloride and bromide, and obtained the values 54·91 and 54·97 respectively.

Purification of Materials.

Water.—All of the water used in either the purification or the analyses was twice distilled, once from a dilute alkaline solution of potassium permanganate and then from a very dilute sulphuric acid solution. Block-tin condensers were used in both distillations, and the apparatus contained no rubber or cork connections. The water was collected, as a rule, in Jena glass flasks, although for special purposes either platinum or quartz receivers were substituted.

Reagents.—Acids and ammonia also were distilled shortly before use, either platinum or quartz condensers and receivers being employed when necessary. Solid reagents were re-crystallised, usually with centrifugal drainage.

Vessels.—Special pains were taken in all the work to prevent the introduction of alkalis or silica into the purest materials, by avoiding as far as possible the use of glass vessels.

Manganous Bromide.—Four different specimens of manganous bromide were employed, which were obtained from different sources, and were purified in different ways. In the case of Samples A and B, purification of the manganese from other heavy metals was accomplished by re-crystallisation of Merck's "chemically pure" potassium permanganate. Sample A was crystallised three times only, while Sample B was thus treated ten times, the last two crops of crystals being thoroughly drained from the mother-liquors by means of a centrifugal.

In order to free the manganese from potassium and convert it into the bromide, the following processes were employed with Sample A:—First the permanganate was dissolved in water, and was reduced by passing sulphur dioxide into the solution. This sulphur dioxide was made by heating copper turnings with concentrated sulphuric acid, and was purified from copper compounds mechanically carried along by passing through three gas washing-bottles, each containing a solution of sulphurous acid, and one column of beads moistened with a similar solution. From the solution of potassium and manganous sulphates the manganese was precipitated by the addition of an alkaline solution of ammonium carbonate. The manganous carbonate was washed with water until the washings were free from sulphates, then it was dissolved in nitric acid, which had been re-distilled until free from chlorine, and the manganous nitrate was re-crystallised six times from a solution strongly acid with nitric acid, four times in a glass vessel, twice in platinum. Usually it was necessary to start crystallisation by inoculation, and cooling with ice was found advisable for the sake of economy in material. From a dilute solution of the purified nitrate in a platinum vessel, the manganese was again precipitated as carbonate, by means of ammonium carbonate which had been freshly made by passing pure carbon dioxide into distilled ammonia in a platinum flask. The resulting manganous carbonate, after thorough washing with water containing a small amount of ammonia to prevent colloidal solution of the

* From the *Journal of the American Chemical Society*, xxviii., No. 11.

carbonate, was readily converted into bromide by solution in hydrobromic acid. Since it was probable that the carbonate contained occluded nitrate, and since a portion of the material had been oxidised to the manganic state during the washing, it was obvious that bromine would be set free during the solution in hydrobromic acid. The use of a platinum vessel for this purpose was therefore precluded. In order to avoid the introduction of silica, instead of glass vessels, quartz dishes were employed. These have been shown to be practically insoluble in acid solutions (Mylius and Meusser, *Zeit. Anorg. Chem.*, 1905, xliv., 221; see also *prox.*). The free bromine was expelled from the solution of manganous bromide by prolonged heating on a steam-bath in a quartz dish. Finally, it was crystallised six times, thrice in quartz, and, after filtration with a platinum funnel, thrice in platinum with centrifugal drainage after each crystallisation. The crystals were dried as far as possible over stick potash in a vacuum desiccator. From the mother-liquors by means of six similar crystallisations, Sample A_2 was obtained.

In the conversion of Sample B from permanganate to bromide minor changes were introduced. The ammonium carbonate was prepared in a pure state by distilling a solution of commercial ammonium carbonate in a platinum still. Instead of expelling free bromine from the solution of manganous bromide by prolonged heating upon the steam-bath, the solution was evaporated as far as possible upon the steam-bath, and the residue was heated to 200° in an electric oven. The bromide was dissolved in water, and after filtration of the solution was crystallised three times in a platinum dish. The third crop of crystals is designated as Sample C_1.

Sample C_1 was prepared from a commercial specimen of pyrolusite. This was first dissolved in hydrochloric acid, and the solution was boiled to expel chlorine. Hydrogen sulphide was passed into the diluted solution of manganous chloride to saturation, and the precipitate of sulphur and sulphides was removed by filtration. After the excess of hydrogen sulphide had been expelled by boiling, the solution was fractionally precipitated with sodium hydroxide until the precipitate was free from iron. Finally, the manganese was precipitated with ammonium carbonate, and the precipitate was washed and dissolved in nitric acid. The nitrate was re-crystallised and converted into bromide exactly as in the case of Sample A.

The source of Sample D was Merck's "chemically pure" manganous sulphate. A solution of 500 grms. of this salt was first saturated with hydrogen sulphide, and the precipitate, which consisted chiefly of manganous sulphide, was removed by filtration. After the addition of a small amount of ammonia, hydrogen sulphide was again passed into the solution to saturation, and the precipitate discarded. In a similar way third and fourth fractions of sulphide were removed. Next the solution was thrice fractionated with small portions of potassium hydroxide, the precipitate being rejected in each case. Then the manganese was twice precipitated as carbonate by means of ammonium carbonate, and the manganous carbonate was converted into bromide exactly as in the case of Sample B. The first crop of thrice re-crystallised bromide is designated Sample D_1, a second similar crop obtained from the mother-liquors is Sample D_2.

(To be continued).

Two New Calcium Ammonium Sulphates.—J. D'Ans.—If a 30 per cent ammonium sulphate solution is boiled with gypsum till the anhydrite disappears, a penta-salt is obtained. It forms refracting prisms and the formula appears to be $(NH_4)_2Ca_5(SO_4)_6 \cdot H_2O$. A second double salt, which is an anhydrous ammonium dicalcium sulphate, is prepared by boiling gyysum in a 40 per cent ammonium sulphate solution. The formula of this is $(NH_4)_2Ca_2(SO_4)_3$. This salt is possibly labile, as in about eight days it gradually decomposes into penta-salt and syngenite. Both salts split up with water, the dicalcium salt forming syngenite in its cooled mother-liquor.—*Ber.*

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

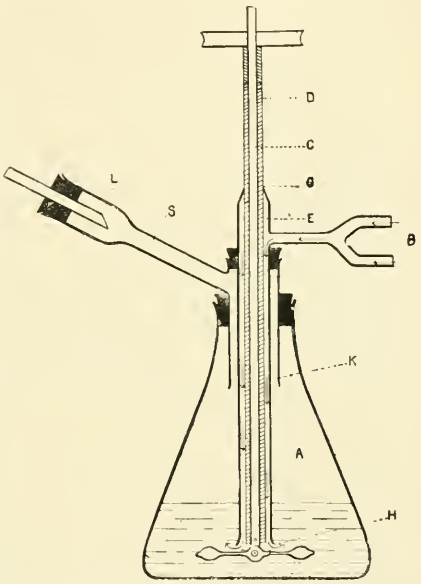
Ordinary Meeting, February 7th, 1907.

Prof. R. Meldola, F.R.S., President, in the Chair.

(Concluded from p. 92).

33. "*A Simple Apparatus, with Stirrer, for Treating a Liquid at its Boiling Point with two or more Gases.*" By Norman Leslie Gebhard.

Whilst studying the action of certain gases on liquids at their boiling points, the apparatus represented in the figure was devised and found very satisfactory.



The liquid is placed in an Erlenmeyer flask A, of capacity appropriate to the volume of liquid under treatment. The rest of the apparatus includes a centrifugal stirrer in the liquid, driven by a water turbine through a horizontal pulley, the rod C carrying the stirrer rotating in an outer tube D. At G, D is sealed into a tube E, of slightly wider bore. The tube E reaches almost to the stirrer and dips well below the surface of the liquid. The gases enter at the tubes B, pass along the annular space between D and E, as indicated by the arrows, and encounter the liquid at H just above the stirrer. The upper part of E is surrounded for part of its length by a wider tube K with a side tube S, through which the vapour of the boiling liquid passes to be condensed in the reflux condenser L. E is fitted to K and the latter to the flask by means of suitable corks. The apparatus enables a liquid, in vigorous ebullition, to be subjected to the action of gases, with constant stirring, and can be constructed without difficulty by anyone with a moderate knowledge of glass-blowing.

34. "*Note on the Arsenates of Lead and Calcium.*" By Spencer Pickering.

Crystallised sodium arsenate of commerce consists of the disodium salt, generally united with 7, but sometimes with 12, molecules of water of crystallisation. In either case, this water may all be expelled at 100°, and decomposition into the pyro-arsenate commences at 150°. The preparations dried at 300° in accordance with the Pharmacopœia are, therefore, overheated. With lead acetate, all commercially pure samples give a precipitate of triplumbic arsenate; but with lead nitrate, the precipitate consists of the diplumbic salt, mixed, occasionally, with a certain amount of the tri- or mono-plumbic arsenates. With preparations of crude sodium arsenate, the amount of lead salt required for precipitation varies considerably, and there is an indication that a compound of the di- and tri-plumbic salts may sometimes be formed.

With calcium chloride or nitrate, sodium arsenate forms the tricalcium arsenate; but, when thus prepared, it is not very insoluble, and is, therefore, unsuitable as an insecticide. But it may be completely precipitated by calcium hydroxide; and thus a mixture of lime and sodium arsenate may be used as a substitute for lead arsenate.

35. "*Camphor-β-sulphinic Acid and Camphorylsulphonium Bases.*" By Samuel and Thomas Percy Hilditch.

Camphor-3-sulphinic acid has been prepared by the reduction with zinc dust of the chloride of Reychler's camphorsulphonic acid. It was further shown that the acid when mixed with a phenolic ether and a dehydrating agent behaves in a similar manner to the aromatic sulphinic acids and yields the camphoryl sulphonium bases. The sulphinic acid and those sulphonium bases which have been prepared exhibit a strong lævorotatory power in distinction from the dextrorotatory sulphonic acid from which they were obtained. With the object of ascertaining whether this change in rotatory power is due to any alteration in structure of the camphor complex, the sulphinic acid was oxidised, and it was found that the products were the original sulphonic acid and *d*-camphoryl-*a*-disulphone. The authors conclude that the above change is probably caused by the conversion of the sulphur from the sexavalent to the quadrivalent state.

36. "*The Condensation of Salicylamide with Aryl Aldehydes.*" By Charles Alexander Keane and William Walter Scott Nicholls.

Benzaldehyde, when heated with salicylamide in presence of hydrochloric acid or of sodium acetate, condenses to form a cyclic compound, in the production of which one molecular proportion of the amide reacts with one of the aldehyde. The substance gives no colouration with ferric chloride, indicating that the hydroxyl group of the salicylamide has participated in the condensation, and it yields an acetyl derivative which is decomposed by concentrated sulphuric acid with the formation of *N*-acetylsalicylamide. It is accordingly regarded as a cyclic compound of the oxazine group, namely, *2-phenyl-1 : 3-benzoxazone*, $C_6H_4\langle^{CO\cdot NH}_{O-CHPh}$; an alternative tautomeric formula is of course also possible. It crystallises from alcohol in silky needles which melt at 169°. On prolonged boiling with water it is gradually decomposed into its constituents; this decomposition is very readily effected by alkalis, less readily by dilute mineral acids. Heated with aniline, benzylideneaniline and salicylamide are formed. The *acetyl* derivative crystallises from alcohol in slender prisms which melt at 88°. It is decomposed into its constituents by heating with dilute alkalis or with dilute mineral acids, and when heated with aniline forms acetanilide, benzylideneaniline, and salicylamide.

2-p-Methoxyphenyl-1 : 3-benzoxazone,—

$$C_6H_4\langle^{CO\cdot NH}_{O-CH\cdot C_6H_4\cdot OMe},$$

is prepared by the condensation of salicylamide with anisaldehyde. It melts at 166—167° and forms an *acetyl* derivative which melts at 91°, and resembles the corresponding phenyl compound in its chemical behaviour.

Benzylidenebis-o-methoxybenzamide—

$$C_6H_5\cdot CH:(NH\cdot CO\cdot C_6H_4\cdot OMe)_2,$$

prepared by the condensation of *o*-methoxybenzamide with benzaldehyde, is much more stable towards alkali than the above cyclic compounds, and is not acetylated by heating with acetic anhydride. It crystallises from alcohol in fine needles melting at 156°.

37. "*The Condensation of Diethylmalonamide with Aldehydes.*" By Harry Burrows and Charles Alexander Keane.

Diethylmalonamide, when heated with benzaldehyde in presence of hydrochloric acid, condenses similarly to salicylamide (Compare Keane and Nicholls, preceding abstract) to form a cyclic compound of the pyrimidine group: *4 : 6-diketo-2-phenyl-5 : 5-diethylhexahydropyrimidine*, $CHPh\langle^{NH\cdot CO}_{NH\cdot CO}\rangle CEt_2$. It crystallises in prisms which melt at 262°; it is stable towards dilute mineral acids, but is decomposed by boiling with sodium hydroxide solution. Heated with acetic anhydride it forms a *diacetyl* derivative which melts at 147° and which is decomposed with elimination of the acetyl groups by treatment with concentrated sulphuric acid.

The corresponding *cinnamyl* compound melts at 241° and also forms a *diacetyl* derivative which melts at 125°.

Chloral-diethylmalonamide, $CEt_2(CO\cdot NH_2)_2,CCl_3\cdot CHO$, is prepared by condensing molecular pyoportions of diethylmalonamide and choral hydrate with hydrochloric acid. It melts at 178° and is stable towards boiling water or hot dilute hydrochloric acid.

OBITUARY.

DEATH OF PROFESSOR HENRI MOISSAN.

The death of Prof. Henri Moissan has robbed the scientific world of one of its most distinguished sons, whose brilliant researches have led to the discovery of many important substances, some of purely theoretical and others of practical interest. Prof. Moissan's name is most widely known in connection with the electric furnace, which he perfected and with which he carried out many fruitful researches. Thus with its aid he succeeded in obtaining temperatures ranging from 3500° to 4000° C., the latter the highest which has yet been reached, and at which he showed that all known elements and compounds may be vaporised. His work on the furnace extended over the years 1892 to 1899, and his text-book, "Le Four Electrique," which described his apparatus and the results of his researches, was translated both into English and German.

One of Prof. Moissan's earliest and most striking achievements was the isolation of fluorine in 1887 by the decomposition by means of a powerful electric current of anhydrous hydrofluoric acid, to which a small quantity of potassium fluoride had been added, and his description of the properties of this element, which up to that time had resisted all attempts to prepare it in the free state, awakened great interest. He subsequently proved the composition of hydrofluoric acid, showing that it is exactly analogous to the acids of the other halogens. His experiments with fluorine further led him to the preparation for the first time of important compounds of it with various elements; for instance, the phosphorus compounds, phosphorus trifluoride and oxyfluoride. Thence he turned his attention to the halogen compounds of boron and silicon, while he devoted much time to the preparation of carbides, some of which, for instance, calcium carbide

have acquired considerable technical importance. The crystalline carbide of silicon or carborundum, which is characterised by its extreme hardness and its resistance to reagents, has found application in the polishing of the hardest kinds of steel and stones, and was also one of Moissan's discoveries, although Acheson had prepared the same compound independently.

The year 1893 saw Moissan's memorable work on the artificial production of the diamond, on which he spent much patient labour. Induced by his study of the decomposition of the fluorides of carbon, which he hoped would lead to the preparation of a crystallised form of carbon, he examined the properties, and more especially the ash, of diamonds from many sources, and was thence led to investigate the action of high temperatures upon various forms of carbon and the separation of the element from fused metals, while the examination of the Cañon Diablo iron, in which "nature seems to have been caught in the act," gave him the final hint. All students of science are familiar with the method by which he made a solution of carbon in fused iron and suddenly cooled it by plunging it into cold water; the sudden cooling and the enormous pressure resulting from the increase of volume undergone by the molten iron as it solidified produced artificial diamonds. In the same year Moissan succeeded in fusing metallic chromium and isolating many compounds of tungsten and molybdenum, while more recently he has described methods of preparing the pentafluoride of iodine by the direct action of fluorine on iodine, and also sulphur hexafluoride, a compound which is interesting in that it demonstrates beyond any doubt the hexavalence of sulphur.

Moissan's researches were confined more especially to inorganic chemistry, which has been greatly enriched by his discoveries; his experimental skill amounted to genius, and his originality and resource were such as to enable him to attack successfully many practical problems which his contemporaries had almost begun to regard as insoluble. His work is a record of victory over apparently insuperable difficulties, and he forced the most refractory and unmanageable of substances to yield to his mastery. He was perhaps the greatest of the French school who have devoted themselves to the synthesis of minerals with such brilliant results, and his untimely death has brought to a sudden end labours unequalled in the regions of chemical mineralogy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 6, February 11, 1907.

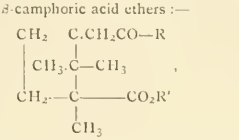
Preparation of the Acylcampholic Ethers, and a New Method of Formation of Phenyloxyhomocampholic Acid.—A. Haller and Charles Weimann.—Cyanocampholic ethers, like all nitriles, react with organomagnesium compounds to give—first, imide compounds, and then, by hydrolysis, ketone derivatives, through the action of dilute sulphuric acid:—

$$C_8H_{14}\begin{cases}CH_2CN\\CO_2R\end{cases} + Mg\begin{cases}R'\\I\end{cases} = C_8H_{14}\begin{cases}CH_2.C\overset{NMgI}{=}R'\\CO_2R\end{cases},$$

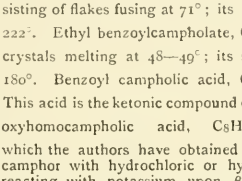
$$C_8H_{14}\begin{cases}CH_2-C\overset{NMgI}{=}R'\\CO_2R\end{cases} + 2H_2O =$$

$$= C_8H_{14}\begin{cases}CH_2.COR'\\CO_2R\end{cases} + Mg\begin{cases}OH\\I\end{cases} + NH_3.$$

Under the conditions with which the authors experimented, the organo-magnesium compound had effect only upon the nitrile group, leaving the COOR group untouched. It was found difficult to saponify these bodies into the corresponding acids, $C_8H_{14}\begin{cases}CH_2COR\\COOH\end{cases}$, since the COOR' group of these ketonic ethers occupies the same position in the molecule as that ascribed to the same group in the β-camphoric acid ethers:—



The ketonic function of these compounds is readily manifested by the preparation of the semicarbazones. The following bodies are described:—Methyl acetylcampholate, $C_8H_{14}\begin{cases}CH_2CO.CH_3\\CO_2CH_3\end{cases}$, a colourless oil distilling at 190° under a pressure of 50 mm.; its semicarbazone, $C_{14}H_{25}O_3N_3$, fine white needles melting at 251°. Ethyl propionylcampholate, $C_8H_{14}\begin{cases}CH_2.CO.CH_2.CH_3\\COOC_2H_5\end{cases}$, a yellowish oil distilling at 198° under 25 mm.; its semicarbazone, $C_{16}H_{29}O_3N_3$, fine silky needles melting at 180·5°. Methyl benzoylcampholate, $C_8H_{14}\begin{cases}CH_2.CO.C_6H_5\\CO_2CH_3\end{cases}$, consisting of flakes fusing at 71°; its semicarbazone melts at 222°. Ethyl benzoylcampholate, $C_8H_{14}\begin{cases}CH_2.CO.C_6H_5\\CO_2C_2H_5\end{cases}$, crystals melting at 48—49°; its semicarbazone melts at 180°. Benzoyl campholic acid, $C_8H_{14}\begin{cases}CH_2.CO.C_6H_5\\COOH\end{cases}$. This acid is the ketonic compound corresponding to phenyloxyhomocampholic acid, $C_8H_{14}\begin{cases}CH_2.CHOH.C_6H_5\\COOH\end{cases}$, which the authors have obtained by treating benzylidene camphor with hydrochloric or hydrobromic acid, or by reacting with potassium upon β-brom-benzyl camphor. The compound thus obtained differing from benzylidene camphor by two additional molecules of water and possessing an acid group, may be represented as follows:—



The benzoylcampholate of silver is obtained by double decomposition, as a white precipitate, insoluble in most solvents; the semicarbazone of the acid, $C_{18}H_{25}N_3O_3$, melts at 210°. Phenyloxyhomocampholic acid, $C_8H_{14}\begin{cases}CH_2.CHOH.C_6H_5\\COOH\end{cases}$, prepared by reduction of benzoyl campholic acid with sodium amalgam. It was found that an identically similar body was produced by hydrating benzylidene camphor, and its formula as that of an ϵ-oxyacid is well established. Its melting-point is 200° to 202°.

Various Syntheses of Dimethyl Isopropyl Carbinol, $(H_3C)_2.C(OH)—CH.(CH_3)_2$.—Louis Henry.—The author gives an account of various synthetic reactions, which result in the formation of dimethyl-isopropyl carbinol, $(H_3C)_2.C(OH)—CH.(CH_3)_2$. These appear to be accompanied by an intramolecular transposition of elements, which, however, is not borne out by fact and needs explanation; there occur also successive intermediate reactions, which are important to notice. 1. α-Chloroisobutyric aldehyde, $(H_3C)_2—CCl—CH=O$, reacting with magnesium-methyl bromide, produced, not pinacolic alcohol according to expectation, but its tertiary isomer,

dimethyl-isopropyl carbinol, $(H_3C)_2.C(OH)—CH.(CH_3)_2$. The successive steps of the reaction may be explained as follows:—

$$\begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>\!CCl—CH—CH_3 \rightarrow \begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>\!C—CH—CH_3 \rightarrow$$
$$\qquad\qquad O.MgBr \qquad\qquad \backslash O/$$
$$\rightarrow \begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>\!C - CH\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix};$$
$$\qquad\qquad\qquad O.MgBr$$

whence, finally, by the decomposing action of water, dimethyl-isopropyl carbinol is obtained. II. Amylene monochlorhydrin, $(H_3C)_2CCl—CH(OH)—CH_3$, results from the addition of HCl to the oxide of trimethyl-ethylene, $(H_3C)_2—C—CH—CH_3$. The reaction of this product upon magnesium-methyl bromide produces, not, as might be expected, secondary pinacolic alcohol, but its isomer dimethyl-isopropyl carbinol, the course of the reaction being the same as the steps already expressed.

Phenomenon Observed with Regard to a Dissolved Chromic Salt. — Albert Colson. — The author's experiments upon the green polymerised salt, obtained by heating the violet sulphate of chromium, have shown that condensation is more complete at 90° than at 110°. In another series of experiments he has proved that this anomaly is explained by the effect of the solvent upon the bodies once dissolved. The following are the results of observation of the points of solidification of the solutions made at regular intervals:—

Lowering.	Salt obtained at 110°. Solution at 1/10 mol.	Salt obtained at 90°. Solution at 1/10 mol.	Solution at 2/10.
As soon as dissolved	0·29°	0·21°	—
3 hours after	0·35°	0·33°	0·58
6 ,, ...	0·39°	0·38°	—
24 ,, ...	0·415°	0·415°	0·76

Thus the green molecule of chromic sulphate, obtained by heating the violet sulphate above 90°, exists in two states of solution, under the same conditions of temperature and solvent, an initial state of condensation of the form $[Cr_2(SO_4)_3]_2$, and a normal state, $Cr_2(SO_4)_3$, resulting from the slow dissociation of the former. According to van't Hoff's hypothesis, in which the dissolved state is made comparable to the gaseous state, this phenomenon may be compared to the case of a solid, which, reduced to vapour in a determined space, presents two gaseous states at the same temperature. It is the inverse of the vapours of phosphorus and of cyanogen, which correspond to two different solid states, white phosphorus and red phosphorus in the first, paracyanogen and solidified cyanogen in the second case. Polymerisation of the chromic salt is still more marked when the concentration reaches to the melting of the salt in its water of crystallisation. These properties appear common to all green sulphates prepared in the cold.

Alcoholisation of Metallic Cyanides.—H. Guillemard. —In a long series of experiments the author has investigated the variation as a function of the temperature and duration of the reaction, in the quantities of nitrile and carbylamine formed, when alcoholising agents, such as iodides, alcoholic sulphates, and sulphovinates, are made to react upon different cyanides. The general conclusion drawn from the facts obtained is that the cyanides thus treated yield, at a low temperature carbylamines, at a higher temperature a mixture of carbylamine and nitrile, and above a certain temperature nitriles only. Thus, at a low temperature the cyanides correspond to the formula MNC. The formation of nitriles at a higher temperature may be explained by several hypotheses; either the constitution of the cyanides becomes modified, the molecules in increasing number taking the formula MCN, and becoming an allotropic mixture whose state of equilibrium is a function of the temperature; or, the constitution of the cyanides remaining unaltered, they react differently at different temperatures; or, finally, the carbylamine, which alone is produced at a low temperature, isomerises at a higher temperature, to adopt the more stable constitution of ordinary nitriles. All points to the latter hypothesis being the correct one, it having been proved that carbylamines isomerise very readily.

Catalytic Hydrogenation of the Non-saturated Ether Salts.—G. Darzens.—A general method of synthesis of the saturated ketones, $C_nH_{2n}O$, by the catalytic hydrogenation of the non-saturated ketones, $C_nH_{2n-2}O$, having been already described, the author now applies the same method, in another series, to the synthesis of saturated bodies, viz., the preparation of saturated acids from the ethers of the non-saturated ethylene acids $C_nH_{2n-2}O_2$. I. *Fatty Series.*—A whole series of $\beta\beta$-methyl-alkyl-acrylic ethers of the type $\begin{matrix} R \\ CH_3 \end{matrix}\!\!>\!C=CH—CO_2C_2H_5$ gave rise to fatty acids of the general formula $\begin{matrix} R \\ CH_3 \end{matrix}\!\!>\!C—CH_2—CO_2C_2H_5$. II. *Aromatic Series.*—The catalytic hydrogenation of the cinnamic ethers readily produced the corresponding phenylpropionic ethers. III. *Hydroaromatic Series.*—$\Delta(1.2)$-Tetrahydrobenzoic acid was obtained from cyclohexanone; also hexahydrophenylacetic acid, and their methods of preparation are described. The experimental results show clearly the difference existing between catalytic hydrogenation and that effected by sodium in presence of boiling alcohol. The latter transforms the group —COOR into $—CH_2OH$, frequently also reacting with the aromatic radicals and ethylene groups in the $\alpha\beta$-position. Catalytic hydrogenation, on the other hand, generally leaves untouched the aromatic radicals and the COOH group, whilst the ethylene groups is always hydrogenated, whatever its position. These methods give a practical means of effecting the synthesis of an acid of the type C_{n+2}, starting from an aldehyde or ketone of the formula C_n.

Transformation of the Primary Saturated Alcohols into the Corresponding Monobasic Acids.—H. Fournier.—The author has effected the transformation of the primary saturated alcohols into monobasic acids possessing the same number of carbon atoms, by means of alkaline potassium permanganate, instead of the chromic mixture ordinarily used, which, being acid, always produces a large proportion of aldehyde or ether salt. It has hitherto been believed that the use of alkaline potassium permanganate gives only a very small yield of the monobasic acid, but it is now proved that under suitable conditions a very good yield is obtained, varying from 70 per cent to 75 per cent.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 1, 1907.

Intermediate Products in Alcoholic Fermentation.—Arthur Slator.—The author has shown that lactic acid is not an intermediate product in the fermentation of glucose by means of yeast to alcohol and carbon dioxide. For, in the first place, lactic acid is either not destroyed by yeast or only very slowly and incompletely, whereas if it is an intermediate product it must disappear as quickly as it is formed, or else it would be found in the solution; secondly, lactic acid when added to a fermenting liquid retards fermentation slightly instead of increasing it; and, lastly, although small quantities of lactic acid have been isolated during fermentation, this fact cannot be adduced as an argument that it is an intermediate product, and it is much more probable that it is a by-product. If an intermediate product does exist it must satisfy the following conditions:—(1). It must ferment at least as quickly as, and perhaps much more quickly than, glucose; (2) it must disappear quickly when introduced into a fermenting solution; and (3) it must be difficult to isolate it from such a solution.

Sulphur Dye-stuffs.—H. Wichelhaus.—Many natural dye-stuffs, such as brazilin, hæmatoxylin, maclurin, euxanthone, can be converted into sulphur dye-stuffs by the following method:—Three parts of the substance are heated to 250—300° with six parts of sulphur. Evolution of sulphuretted hydrogen proceeds vigorously for six to eight hours. The product is dissolved in caustic soda, and precipitated with acid; then it is heated to 120° to convert the amorphous sulphur into the soluble modification, and the latter is removed by means of carbon disulphide. The same process can be carried out with artificial dye-stuffs which possess a phenol character, such as fluorescein, and in this case there is no need to prepare the fluorescein beforehand, for the sulphur dye is obtained if phthalic acid, resorcin, and sulphur are fused together. The dye thus prepared appears to differ from Gattermann's thio-fluorescein, but as its analysis presents great difficulties the author does not feel justified in drawing any definite conclusions as to its composition.

Relative Stability of some Metallic Amine Derivatives.—L. Tschugaeff.—The investigation of the formation of amine derivatives of copper, silver, platinum, and nickel has shown that the power of the amines to form complexes is dependent upon the number of unsubstituted hydrogen atoms. By the replacement of the first ammonia hydrogen by an alkyl the proportions seems to be but little changed, but when the substitution process has been repeated the power of forming complexes is greatly affected, and is destroyed by the replacement of the third ammonia hydrogen. The power of forming complexes is a property of many amines of different affinity constants; and, moreover, two amines which have almost the same affinity constants, *e.g.*, ethylamine and tripropylamine, behave differently as regards the formation of complexes. Hence the power is influenced not only by the basic properties of the ammonia or amine nitrogen, but also by other factors.

Chromium Boride.—E. Wedekind and K. Fetzer.—Hitherto no boride of chromium of definite composition has been described, although the preparation of such a compound would be of interest in view of the fact that borides of iron, cobalt, and nickel of the formula MeB have been obtained. The reason for this is that it is extremely difficult to prepare a pure chromium boride by the usual method of heating the constituents, or a mixture of boron and chromium oxide in the electric furnace, because the carbon vapour from the electrodes is taken up by the fused product, some of it being combined, while the rest separates out on cooling as graphite. The authors' method does away with this difficulty. They allowed the liquefied metal formed from chromium thermite to act on the calculated amount of boron. The latter was prepared by Moissan's method from boric acid anhydride and magnesium. Before the beginning of the experiment the chromium thermite was converted into a pulp with liquid air. Then amorphous boron was placed at the bottom of a Hessian crucible, covered with chromium thermite, and then with the above thick liquid. Then a mixture of barium peroxide and aluminium was mixed with this upper layer. The reaction was violent, and, after cooling, the regulus was broken up in a steel mortar and treated with warm dilute hydrochloric acid to remove the excess of uncombined chromium, then with nitric acid, and finally with aqua regia. After washing with water and drying, a silver-white crystalline powder was obtained. Chromium boride is characterised by its extraordinary resistance to acid and alkaline reagents. Even hydrofluoric acid and mixtures of hydrofluoric and nitric acid have no effect upon it, and the authors found that sodium peroxide is the only substance which would decompose it into its constituents. For the analysis the compound was heated in a silver crucible with sodium peroxide, chromate and borate being formed. The melt was boiled with water and the chromium oxide filtered off. To the clear filtrate some drops of helianthin and hydrochloric acid were added, till the reaction was neutral. After cautiously heating for some time on the water-bath (to drive off carbon dioxide) about one-third of the total volume of pure glycerin was added, with some drops of phenolphthalein, and then the liquid was titrated with N/10 sodium hydroxide. The chromium hydroxide filtered off was dissolved in hydrochloric acid, precipitated with ammonia, washed, and ignited. The chromium boride was not quite pure, but contained some uncombined metal; nevertheless, there could be no doubt from the analysis that it has the simple formula CrB, corresponding to FeB, CoB, NiB, and MnB. Its specific gravity is 5·4 at 17°. It conducts an electric current, and is very hard, scratching glass and quartz easily. It is fusibly only with difficulty, and can be heated to a red heat in a current of oxygen for some time without undergoing any alteration. Hydrochloric acid gas acts upon it only very slowly. It possesses ferro-magnetic properties, and is attracted by a powerful electro-magnet.

Products obtained from the Carbonates of the Alkaline Earths, Carbon, and Nitrogen.—O. Kuhling.—The author has determined the relative quantities of cyanide and cyanamide formed when carbon and nitrogen act upon the carbonates of the alkaline earths at temperatures from 900° to 1400°. He used one molecule of the pure carbonate to three atoms of sugar carbon, and exposed the mixture to the action of nitrogen. The cyanide was determined by Feld's method, and the cyanamide by a modification of Perotti's process with ammoniacal silver solution. The experiments show that the tendency to absorb nitrogen is greatest in the case of barium carbonate and less with strontium carbonate, while calcium carbonate only absorbs traces. The mixture containing barium carbonate forms chiefly cyanide, and the calcium carbonate mixture cyanamide salt, while the strontium salt occupies an intermediate position. The addition of the corresponding chlorides increases the absorption of nitrogen, but in the case of the barium salt this increase is effected only by small amounts of chloride, and in the presence of larger quantities the percentage of nitrogen absorbed again decreases. If the nitrogen is charged with water-vapour, the temperature necessary for the reaction is increased and the yield reduced.

Carbon Suboxide (II.).—Otto Diels and George Meyerheim.—Further researches have shown that not only malonic acid diethyl ester, but also the dimethyl, dibenzyl, and diphenyl esters yield carbon suboxide when treated with phosphorus pentoxide. Methenyl tricarbonic ester acts similarly:—

$$CH(CO_2C_2H_5)_3 = 3C_2H_4 + CO_2 + 2H_2O + OC{:}C{:}CO.$$

Also free malonic acid itself, when heated with phosphorus pentoxide, is converted into the suboxide—

$$CH_2(COOH)_2 = 2H_2O + OC{:}C{:}CO,$$

and simultaneously carbon dioxide and acetic acid are formed, $CH_2(COOH)_2 = CH_3.COOH + CO_2$. The yield from malonic acid is about 10 to 12 per cent of the theory, and this method of preparing the suboxide is more convenient than using the ester, and was therefore employed for the authors' subsequent experimental work. Twenty grms. of pure finely-powdered malonic acid are thoroughly mixed with 200 grms. of phosphorus pentoxide in a large dry flask, which is connected first with a vessel cooled by means of ice and salt and then with a vessel cooled by liquid air. The whole apparatus is exhausted to about 0·1 to 0·2 mm. pressure, and then the flask containing the mixture is placed in an oil-bath heated to 140—150° for three-quarters of an hour. The vessel cooled with liquid air then contains a white mass consisting of carbon dioxide and suboxide. The former is slowly driven off by placing the vessel in an empty Weinhold's vessel, and then the suboxide can be allowed to boil off at the ordinary temperature into a cooled receptacle. The acetic acid formed is generally converted by means of the carbon

dioxide into other compounds. The melting-point of carbon suboxide is -107^{5}, and its specific gravity in the liquid state is 1·11 at 0°. At low temperatures (0—15°) the suboxide is converted into a polymer or mixture of polymers, while at higher temperatures gaseous products are formed, among which carbon monoxide and dioxide are found, and a residue of composition varying according to the transition temperature is left. If the polymer $(C_3O_2)_x$, prepared at a low temperature, is heated, carbon dioxide, carbon monoxide, and carbon suboxide all result, the last named in fairly large quantities. The residue, even when heated to a red heat, does not consist of carbon, but has the composition of a carbon oxide very poor in oxygen. The polymer very readily takes up water in the air, and carbon dioxide is split off. When cold water is added to the polymer, a development of heat occurs, carbon dioxide is evolved, and an eosin-red solution is produced. The authors think that the physical constants of the suboxide all show that the formula is OC:C:CO.

MISCELLANEOUS.

Society of Arts.—*Prize for Industrial Hygiene.*—The Council of the Society of Arts are prepared to award, under the terms of the Benjamin Shaw Trust, a Gold Medal, or a prize of £20. The Medal, under the conditions laid down by the testator, is to be given "For any discovery, invention, or newly-devised method, for obviating or materially diminishing any risk to life, limb, or health, incidental to any industrial occupation, and not previously capable of being so obviated or diminished by any known and practically available means." Intending competitors should send in descriptions of their inventions not later than December 31st, 1907, to the Secretary of the Society of Arts, Adelphi, London, W.C. Such descriptions may be sent in under the inventor's name, or under a motto, accompanied by a sealed envelope, enclosing the name, as preferred. The Judges will be appointed by the Council. The Council reserve the right of withholding the prize or of awarding a smaller prize or smaller prizes, if in the opinion of the Judges nothing deserving the full award is sent in.

Merchant Venturers' Technical College, Bristol.—Since the disastrous fire which partially destroyed the main building of this College in October last, a Committee of the Society of Merchant Venturers has had under consideration the course which it should recommend the Guild to adopt. Various sites for the re-erection of the College have been suggested and carefully discussed, and a report has now been submitted to the Society advising the retention of the present site, which is particularly central, close to the tramway terminus, and within easy reach of the three principal railway stations of Bristol. At a general meeting held on Friday last this report was received and unanimously adopted, and steps will therefore be taken at once to replace the various laboratories, workshops, lecture theatres, &c., with all possible speed. Little time has been lost since the building was handed over to the Merchant Venturers by the firm in charge of the salvage arrangements, as the interval has been utilised to clear the building of *débris* and to remove certain weak portions of the walls. In framing plans for re-building, the Merchant Venturers will bear in mind the possibility that at some future period the College may be called upon to take its proper part in the formation of the proposed University of Bristol.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Society of Arts, 8. (Cantor Lectures). "Romanesque Ornament," by F. Hamilton Jackson.
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Exhibition of a Gas Calorimeter," by Prof. C. V. Boys. "Four Years' Experience in Metering Producer Gas, and Continuously Recording its Calorific Power," by Prof. R. Threlfall.

TUESDAY, 5th.—Royal Institution, 3. "The Visual Apparatus of Man and Animals," by Prof. William Stirling.
—— Society of Arts, 4.30. "British Malaya," by Sir William Hood Treacher.

WEDNESDAY, 6th.—Society of Arts, 8. "The Discovery of the South Eastern Coalfield," by Prof. W. Boyd Dawkins.
—— Society of Public Analysts, 8. "Disposition and Analyses of Sewage Matters Deposited on Superposed Surfaces," by W. J. Dibdin. "Composition of Milk," by H. Droop Richmond. "Preservatives in Milk and Milk Products," by H. Droop Richmond and E. H. Miller.

THURSDAY, 7th.—Royal Institution, 3. "Old Dutch Painting and Painters," by Dr. W. Martin.
—— Chemical, 8.30. "Constitution of Chaulmoogric and Hydnocarpic Acids," by M. Barrowcliff and F. B. Power. "Volume Changes which accompany Transformations in the System $Na_2S_2O_3,5H_2O$," by H. M. Dawson and C. G. Jackson.

FRIDAY, 8th.—Royal Institution, 9. "Certain Seasonal Diseases of the Sheep, and the Means of Preventing them," by Prof David J. Hamilton.
—— Physical, 8. "Rate of Recovery of Residual Charge in Electric Condensers," by Prof. Trouton and Mr. Kuss. "Experimental Mathematics," by Mr. Pichon. "An Instrument to Describe Families of Equiangular Spirals," by Mr. Blakesley. "A Micromanometer," by Mr. Roberts.

SATURDAY, 9th.—Royal Institution, 3. "Röntgen, Cathode, and Positive Rays," by Prof. J. J. Thomson.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2467.

ON A NEW IRON CARBONYL, AND ON THE ACTION OF LIGHT AND OF HEAT ON THE IRON CARBONYLS.*

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S., Jacksonian Professor in the University of Cambridge, and HUMPHREY OWEN JONES, M.A., D.Sc., Fellow of Clare College, and Jacksonian Demonstrator in the University of Cambridge.

(Concluded from p. 99).

Decompositian of Iron Pentacarbonyl Absorbed in Alumina.

During the course of some experiments on the absorbing power of various substances for gases and vapours, it was found that alumina absorbed 2·5 per cent of its weight of iron pentacarbonyl from gases saturated with the vapour at the ordinary temperature. On exposing this alumina to light (out of contact with air) it became coloured—first pink, then red, reddish purple, and finally a dark reddish purple. Experiments showed that during this action carbon monoxide was evolved in approximately the theoretical quantity, if care were taken to shake the alumina frequently so as to expose it all to light.

The solid diferro-nonacarbonyl formed in the alumina possibly forms a kind of "lake" with the alumina. The coloured alumina retains its colour when boiled with pyridine, although alumina will not remove the colour from the red pyridine solutions of diferro-nonacarbonyl. Warm concentrated hydrochloric acid removes the colour, gas is evolved, and ferrous chloride is formed; nitric acid reacts with the coloured alumina in the cold, but sulphuric acid has very little action on it.

Action of Heat on Diferro-nonacarbonyl.

As stated by Mond and Langer, and confirmed in our previous communication, the solid, when heated alone, breaks up into iron pentacarbonyl, iron, and carbon monoxide. It was observed that the iron pentacarbonyl so produced was coloured green, but that when distilled the green colour was removed from it. This decomposition occurs at about 95° C.

Quantitative experiments were made in which a weighed quantity of the solid was placed in a porcelain boat and heated in a stream of hydrogen to a temperature of about 100° to 120° C. by means of a toluene- or an air-bath; the volatile iron pentacarbonyl was thus carried off as vapour and passed through a glass tube, bent twice on itself and heated in an air-bath to a temperature of about 200° C. The boat and the coiled tube were weighed after the experiment, and so the amount of left iron and the amount of iron deposited from the volatile carbonyl were determined. The boat was then heated in a current of oxygen until there was no further change of weight, and so a second determination of the iron made as ferric oxide.

The following are typical experiments performed in this way:—

Grm.		Grm.		Grm.	
0·2981	$Fe_2(CO)_9$ gave	0·0754	Fe in tube and	0·0223	Fe in boat
0·4505	,,	0·1211	,,	0·0378	,,
0·6555	,,	0·1215	,,	0·0725	,,

It is evident that this method does not give consistent results, and even if it did it would probably give values for the iron deposited in the bent tube from the iron pentacarbonyl that were too high, since it has been shown that the iron so deposited always contained carbon.

* A Paper read before the Royal Society, January 24, 1907.

Other experiments were then made in which the iron pentacarbonyl was collected and weighed.

A weighed quantity of diferro-nonacarbonyl was placed in one limb of a U-shaped tube, which was then exhausted and sealed. This limb of the tube was heated and the iron pentacarbonyl which was formed was condensed in the other limb by cooling this in liquid air. The iron pentacarbonyl and the residue left in the other limb of the tube were weighed. The residue was found to be iron in such a finely-divided state that it was pyrophoric.

The following experiments are typical. In the first experiment the solid was heated to 100° C. and in the second to 110° to 115° C.

Grm.		Grm.		Grm.	
0·685	$Fe_2(CO)_9$ gave	0·567	$Fe(CO)_5$ and	0·055	Fe
0·587	,,	0·453	,,	0·039	,,

In the former communication it was stated that the decomposition might be represented by the equation $2Fe_2(CO)_9 = 3Fe(CO)_5 + Fe + 3CO$.

The above results confirm this, since the amounts of $Fe(CO)_5$ formed on this view would be 0·583 and 0·503 grm. respectively, and the amounts of iron would be 0·053 and 0·045 grm. respectively.

Since it is shown later that, by the action of heat on diferro-nonacarbonyl in presence of solvents below 100° C., a compound, $Fe(CO)_4$, is produced, it is quite possible that the decomposition was produced in two stages, represented by the equations $2Fe_2(CO)_9 = 2Fe(CO)_5 + 2Fe(CO)_4$ and $2Fe(CO)_4 = Fe(CO)_5 + Fe + 3CO$.

This view is supported by the fact that when diferro-nonacarbonyl is heated to 100° C. in a tube filled with carbon dioxide and fitted with a small mercury index manometer, at first the solid is decomposed with formation of a green liquid without any appreciable development of pressure, but as the heating is continued, pressure is gradually developed, iron is formed, and the green colour disappears.

When heated to 100° C. with carbon monoxide under a pressure of 75 atmospheres, the solid is at once converted into liquid iron pentacarbonyl and no green colour is produced. This shows that the re-combination of carbon monoxide with the diferro-nonacarbonyl is favoured by pressure, and the formation of the green compound usually produced is prevented in this way.

These facts are here re-stated and supported by further evidence in order that they may be compared with the results of experiments on the action of heat on diferro-nonacarbonyl in the presence of solvents.

When the crystals of diferro-nonacarbonyl are heated with a solvent such as ether or toluene, change begins at a much lower temperature, below 60° C., and the liquid acquires a dark green colour (as stated above, the green colour is developed slowly, even at 46° C.). When enough of the solvent is present, the whole of the solid dissolves and no iron or other solid substance is produced; the solution has such an intense colour that it is opaque, except in very thin layers.

It is clear, therefore, that we have here a different reaction to deal with.

The green solutions, on exposure to light, lose their colour and deposit the orange crystals of diferro-nonacarbonyl and a small quantity of a black solid.

By carrying out experiments in a closed tube filled with inert gas and fitted with a mercury manometer, it was shown that no change of pressure was caused by the action of heat or diferro-nonacarbonyl; hence no gas can have been evolved. Long continued heating, however, causes a disappearance of the green colour, and slight pressure is developed.

Similar results were obtained when benzene, petroleum ether, brombenzene, or iron pentacarbonyl was used as solvent.

When pyridine, alcohol, acetone, or acetonitrile was used as solvent, the solution obtained was not green, but

some shade of red or brownish red, but again no gas was evolved.

When nickel carbonyl was used as solvent, the solution obtained was yellow, with only the faintest trace of green colour, a black solid was left, probably iron, and gas was evolved.

With chloroform, ferrous chloride was produced, so that the solvent had entered into the reaction; solid products were also produced when nitrobenzene was used as solvent, and with ethyl acetate or methyl aniline a greenish brown solution and a solid were produced.

The green solutions in toluene, ether, or petroleum ether were found in some cases to deposit beautiful green crystals, which, when separated, were found to contain iron and carbon monoxide and to re-dissolve in the solvent to give a green solution.

After numerous trials, the best conditions for the separation of the maximum amount of these crystals were found, and the following summarises the process used for their preparation.

The solid diferro-nonacarbonyl was sealed up in a tube, the air from which had been displaced by carbon dioxide, with toluene in the proportion of 1 grm. of the carbonyl to 20 cc. of toluene. The tube was then heated gradually, with occasional shaking, to about 95° C., and kept at that temperature until all the reddish yellow solid had disappeared, the tube being meanwhile shaken from time to time. If shaking is omitted or if the tube be heated to too high a temperature or for too long a time, a quantity of dark coloured powder is formed, but with care this may be almost entirely avoided.

The tube is then allowed to cool slowly, when fairly large crystals of the green compound separate from the solution and, after washing with the solvent and drying in a desiccator, were used for analysis.

The yield of the green crystals obtainable is only about 20 per cent by weight of the diferro-nonacarbonyl used.

The carbon monoxide was determined by combustion, care being taken to heat the boat long enough to oxidise any carbon that may have been retained in the iron. In this case the iron almost entirely remains in the boat, and, in some cases when there was no observable loss, good determinations of the percentage of iron were obtained by weighing the ferric oxide; in other cases there was obviously a loss, indicated by deposition of iron on the combustion tube near the boat, and the percentage of iron was low. Independent determinations of the iron were made by decomposing a weighed quantity of the crystals with nitric acid and igniting.

The following results were obtained by these methods:—

	Grm.		Grm.		Grm.
1.	0·1078	gave	0·1118	CO_2 and	0·0513 Fe_2O_3.
2.	0·1214	,,	0·1258	,,	0·0442 ,,
3.	0·1744	,,	0·0845	Fe_2O_3.	
4.	0·1828	,,	0·0868	,,	

	Found.	
	CO.	Fe.
1.	66·1	33·3
2.	65·9	—
3.	—	33·9
4.	—	33·2
$Fe(CO)_4$ requires	66·66	33·33

The compound is, therefore, *iron tetracarbonyl* or some polymer of this.

The decomposition of diferro-nonacarbonyl in presence of solvents such as toluene and ether is probably to be represented by the equation $Fe_2(CO)_9 = Fe(CO)_5 + Fe(CO)_4$.

Further evidence in support of this was obtained by carrying out the decomposition in tubes filled with carbon dioxide and fitted with a mercury manometer. No change of pressure was produced by the decomposition. On exposing the tubes, after heating and now containing a green solution, to light, the orange crystals of diferro-nonacarbonyl were deposited and pressure was produced, showing that during the action of heat iron pentacarbonyl has been produced.

Iron tetracarbonyl crystallises in short, dark green, lustrous prisms, the density of which was determined by the flotation method in a mixture of ethylene dibromide and alcohol, in both of which the compound is almost insoluble and was found to be 1·996 at 18° C.; the molecular volume is therefore 84. If we suppose that a molecule of $Fe_2(CO)_9$ (molecule volume 174) decomposes into a molecule of solid iron pentacarbonyl (molecule volume 128) and a molecule of the new iron tetracarbonyl, 174 volumes become 212 and there is consequently an expansion of 28 volumes, or about 16 per cent.

Iron tetracarbonyl is a substance of remarkable stability. On heating to about 140° to 150° C. it decomposes into carbon monoxide and iron. When heated under a pressure of 150 atmospheres of carbon monoxide it underwent no visible change until a temperature of 129° C. was reached, and then only turned slightly brown; it was not found possible to re-convert it into iron pentacarbonyl.

Reactions of Iron Tetracarbonyl.

The compound is not attacked by a concentrated solution of hydrochloric acid even on boiling; it is attacked by cold concentrated nitric acid, but only by concentrated sulphuric acid when heated. In the last case carbon monoxide and *ferrous* sulphate are produced. Aqueous solution of alkalis, whether hot or cold, had only a very slight action on the compound.

Molecular Weight.

Iron tetracarbonyl is soluble in many organic solvents, to which it imparts an intense colour; as it appeared to be decidedly soluble in benzene, it was thought that a molecular weight determination might be made by the cryoscopic method.

On examining the solubility, however, it was found to be small, only about 4 per cent in benzene and much less in acetic acid and alcohol.

Attempts were, however, made to determine the molecular weight, and proved definitely that the molecular weight must be very high.

For instance, a solution of 0·031 grm. of the compound in 12·88 grms. of benzene had a freezing point only 0·003° C. below that of the solvent.

Now if the molecule were $Fe(CO)_4$,(168) the depression of freezing point should be 0·076° C., so that the molecule would appear to be of the order of $\{Fe(CO)_4\}_{20}$, or, at any rate, the compound is a polymer consisting of many $Fe(CO)_4$ units.

Behaviour of Iron Tetracarbonyl towards Solvents.

Iron tetracarbonyl dissolves in benzene, toluene, petroleum ether, ether, acetonitrile, ethyl acetate, methyl and ethyl aniline, acetone, nickel carbonyl, and iron pentacarbonyl to give solutions of a dark green colour.

It is much less soluble in ethyl acetate and ether than in the hydrocarbons and carbonyls.

The solutions in the above solvents are all stable to heat at 100° C. for short periods, but the colour gradually disappears and iron is deposited if the heating be long continued. This decomposition is quickly completed at 140° C.

The iron tetracarbonyl can be re-crystallised easily from toluene, petroleum ether, or nickel carbonyl, when due care is taken to prevent oxidation, to which the solutions are very sensitive.

Pyridine, on the other hand, dissolves iron tetracarbonyl quickly and gives a green solution, which on standing for a few minutes turns red, which change of colour is brought about rapidly by warming.

Alcohol behaves similarly; only a faint green colour is obtained, as the substance is very sparingly soluble in alcohol; this solution becomes red on boiling. Solutions of the iron tetracarbonyl in the solvents, in which it forms

green solutions when mixed with pyridine in sufficient quantity, turns red on standing.

It is probable, therefore, that the iron tetracarbonyl when dissolved in pyridine exists in a different molecular state from that in which it exists in the green solutions, that is, it is dissociated into simpler molecules or is combined with the solvent. The same is true of solutions in alcohol. Now it was found that acetonitrile and acetone also gave red solutions instead of green when heated with the diferro-nonacarbonyl. Presumably the iron tetracarbonyl is present in these solutions in the same molecular state as in the pyridine solutions, but the effect of these solvents is only strong enough to bring about the conversion of iron tetracarbonyl into this state at the moment of its formation and not at a later stage.

It is noteworthy that iron tetracarbonyl dissolved in either nickel carbonyl or iron pentacarbonyl gives a green solution; hence, it follows that this solid iron tetracarbonyl is different from the hypothetical $Fe(CO)_4$, which it was suggested in our former communication (*loc. cit.*, p. 576) was the first product of the action of light on iron pentacarbonyl, and which then combined with this to form $\{Fe(CO)_5Fe(CO)_4\}$ or diferro-nonacarbonyl.

The green solutions of iron tetracarbonyl exhibit a characteristic absorption band in the yellow, while the red solutions show no selective absorption.

Action of Light on Iron Tetracarbonyl.

The green solutions gradually lose their colour on exposure to light, and a metallic looking solid, probably iron, is deposited. The change is very slow and the solutions were too dilute to allow of the detection of evolved gas with certainty: a small amount of a reddish solid, probably ferric oxide, was frequently observed, which was due to oxidation by traces of dissolved oxygen.

The red solution in pyridine appears to be quite stable to light; no change can be observed after long exposure.

A REVISON OF THE ATOMIC WEIGHT OF MANGANESE.*

By GREGORY PAUL BAXTER and MURRAY ARNOLD HINES.

(Continued from p. 103).

Purification of Materials (continued).

Manganous Chloride. — Two samples of manganous chloride were prepared. Sample B corresponded in its purity to Sample B of manganous bromide, since both were made by dissolving the same specimen of manganous carbonate. The solution of the carbonate in hydrochloric acid, which had been distilled with a quartz condenser, was evaporated to dryness in a quartz dish, and was heated to 200° in an electric oven. Then the filtered aqueous solution was evaporated to crystallisation in a platinum dish, and the first crop of crystals was twice re-crystallised (Sample B_1). The mother-liquors also yielded a crop of thrice re-crystallised salt (Sample B_2).

The mother-liquors of the manganous nitrate of Samples B and D were combined and re-crystallised six times, three times in glass and three times in platinum, and from this pure nitrate Sample E_1 of manganous chloride was prepared as above.

Hydrobromic Acid.—Commercial bromine was freed from chlorine by twice converting the bromine into hydrobromic acid by means of thoroughly washed hydrogen sulphide and water, and heating the hydrobromic acid, after distillation, with re-crystallised potassium permanganate. The bromine was thus twice distilled from a bromide, the bromide in the second distillation being almost free from chloride. Iodine was eliminated by boiling the hydrobromic acid in each case with a small quantity of permanganate and rejecting the bromine set free. A portion of the final product, when converted into ammonium bromide by means of ammonia, and added to a solution of 3·46875 grms. (in vacuum) of pure silver, yielded 6·03855 grms. (in vacuum) of fused silver bromide, whence the ratio of silver to silver bromide is 57·443, while 57·445 is the value to be expected (Baxter, "A Revision of the Atomic Weight of Bromine," *Proc. Am. Acad.*, 1906, xlii., 201).

By treating this bromine, covered with water, with washed hydrogen sulphide, hydrobromic acid was again produced. The solution was boiled, after mechanical separation of the greater part of the free sulphur and bromide of sulphur, and was then filtered. In order to remove the sulphuric acid produced during the action of the bromine upon the hydrogen sulphide, the hydrobromic acid was first distilled. Then it was diluted, and a small quantity of re-crystallised barium hydroxide was added to precipitate last traces of sulphuric acid. The slight precipitate of barium sulphate was collected upon a filter, and the acid was three times distilled with rejection of the first and last portions, with a glass retort and condenser. Finally the acid was once distilled with the use of a quartz condenser. The product of the final distillation was collected in quartz vessels, and was used immediately for dissolving the manganous carbonate. That this acid was free from solid impurities, such as alkalis and silica, was shown by evaporating 30 cc. in a weighed platinum crucible. No weighable residue remained after the crucible had been heated to very dull redness.

Hydrochloric Acid.—The "chemically pure" acid was boiled for some time, after the addition of a small quantity of potassium permanganate. Then it was twice distilled in glass, the middle portion only being collected, and finally once in quartz shortly before use.

Nitric Acid.—This acid was twice distilled, all but the last third of the distillate being rejected in each distillation. This acid gave no test for chloride in a nephelometer.

Silver.—Five different specimens of silver were employed, a portion of each one of which had already been used in an atomic weight research, and had been shown to be of the highest grade of purity. Two of these specimens, Samples H and J, were used in an investigation upon the atomic weight of iodine by one of us (Baxter, *Proc. Am. Acad.*, 1905, xli., 78). Sample H was prepared from silver nitrate which had been seven times re-crystallised from nitric acid, five times re-crystallised from water, and finally precipitated with ammonium formate. Sample J was precipitated once as silver chloride, electrolysed once, and finally precipitated with ammonium formate. Sample K was employed in our investigation upon the atomic weight of cadmium (Baxter and Hines, *Journ. Am. Chem. Soc.*, 1905, xxvii., 225). This sample was thrice precipitated as silver chloride, and once electrolysed. Sample L was precipitated once as chloride, once as metal by ammonium formate, and was once electrolysed. This sample has been used in the analysis of cadmium bromide (Baxter, Hines, and Frevert, *Journ. Am. Chem. Soc.*, 1906, xxviii., 770). Sample M was prepared for an investigation upon the atomic weight of bromine, and had been twice electrolysed after a preliminary purification (Baxter, *Proc. Am. Acad.*, 1906, xlii., 207). Samples H, J, and L also were used in the latter research, and were found to give values identical with those obtained with Sample M. All five samples were finally fused in a current of pure hydrogen in a lime-boat. The fused lumps were cleaned with dilute nitric acid, cut into fragments either with a clean steel chisel and anvil, or with a jeweller's saw, treated with dilute nitric acid until free from iron, washed, dried, and finally heated to about 300° in a vacuum.

The Analysis of Manganous Bromide.

The method of analysis was essentially that already frequently employed in this laboratory for the analysis of metallic halides. Weighed portions of the halides, after fusion in hydrobromic or hydrochloric acid, were first

* From the *Journal of the American Chemical Society*, xxviii., No. 11.

titrated against weighed portions of pure silver. Then the precipitated silver salts were collected and weighed.

The apparatus used for the fusion of the manganous bromide in a current of nitrogen and hydrobromic acid gases, was used in the preparation of ferrous bromide by one of us (Baxter, *Proc. Am. Acad.*, 1903, xxxix., 246), and is a modification of apparatus used for a similar purpose in determinations of the atomic weights of cobalt (Richards and Baxter, *Proc. Am. Acad.*, 1897, xxxiii., 117), nickel (Richards and Cushman, *Proc. Am. Acad.*, 1897, xxxiii., 99), and uranium (Richards and Merigold, *Proc. Am. Acad.*, 1902, xxxvii., 378) in this laboratory. A mixture of air and ammonia was passed over heated rolls of copper-gauze, and the excess of ammonia was removed by means of sulphuric acid. The gas was then purified and dried in an apparatus constructed wholly of glass, with ground joints, which consisted of a tower filled with beads moistened with silver nitrate solution to remove sulphur compounds, two similar towers containing dilute sulphuric acid to eliminate last traces of ammonia, and two towers filled with granular fused potassium hydroxide to absorb moisture and carbon dioxide. The partially dried gas, after bubbling through pure bromine in a small flask, passed into a second flask containing hydrobromic acid in which washed red phosphorus was suspended to convert the bromine into hydrobromic acid. A U-tube, also containing red phosphorus and hydrobromic acid, removed traces of bromine which escaped reduction in the flask. Two additional U-tubes containing beads moistened with concentrated hydrobromic acid only, served to eliminate phosphorus compounds which, in the investigation upon ferrous bromide (*loc. cit.*), were found to accompany the hydrobromic acid if the phosphorous acid in the reduction was allowed to become very concentrated. Finally the mixture of nitrogen and hydrobromic acid gases was thoroughly dried, first by pure fused calcium bromide, and then by re-sublimed phosphorus pentoxide.

The manganous bromide, contained in a weighed platinum boat, was heated gently in a current of nitrogen, purified as above, and dried by phosphorus pentoxide, until the greater part of the crystal water was expelled, then strongly in a current of nitrogen and hydrobromic acid until fused. After the salt had cooled, the hydrobromic acid was displaced by nitrogen, and this in turn by air which had been passed over solid potassium hydroxide, concentrated sulphuric acid, and phosphorus pentoxide. As stated before, the purifying apparatus was constructed wholly of glass, in such a way that by means of stopcocks any one gas or mixture of gases could be employed, to the exclusion of the others. The boat was then transferred to the weighing-bottle in which it was originally weighed, and the stopper was inserted without an instant's exposure of the salt to moisture, by means of the bottling apparatus which has been frequently described in papers from this laboratory (Richards and Parker, *Proc. Am. Acad.*, 1896, xxxii., 59). The weighing-bottle was then allowed to stand in a desiccator near the balance case for some time before it was weighed.

Next the boat was transferred to a flask, and the salt was dissolved in about 300 cc. of the purest water. The weighing-bottle was rinsed, and the rinsings were added to the solution. Then the solution was filtered into the glass stoppered precipitating flask through a tiny filter to collect a trace of insoluble matter, and the filter-paper and residue were ignited in a weighed porcelain crucible.

From the weight of manganous bromide very nearly the requisite quantity of pure silver could be calculated. This silver was weighed out and dissolved, in a flask provided with a column of bulbs to prevent loss of silver by spattering, in distilled nitric acid diluted with an equal volume of water. After the silver was dissolved, the solution was diluted to twice its volume, and was heated until free from nitrous fumes. Then it was still further diluted until not stronger than 1 per cent, and was slowly added with constant stirring to the 1 per cent solution of manganous bromide in the precipitating flask. After having been shaken for some time, the solution was allowed to stand several days, one week in the case of Analyses 14 and 15, with occasional shaking, until the supernatant liquid was clear. Thirty cc. portions of the solution were then tested with hundredth-normal solutions of silver nitrate and sodium bromide in the nephelometer for excess of bromide or silver, and, if necessary, either standard silver nitrate or sodium bromide solution was added, and the process of shaking and testing repeated, until the amounts of bromide and silver in the solution were equivalent. If the solution was perfectly clear when tested, and contained no considerable excess of bromide or silver, the test solutions were discarded, since they contained only negligible amounts of silver bromide, otherwise they were returned to the flask, and a correction was applied for the silver bromide thus introduced.

As soon as the exact end-point of the titration had been found, about .4 centigrms. of silver nitrate in excess were added to precipitate dissolved silver bromide, and the flask was again shaken, and allowed to stand until clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible after it had been washed with water by decantation about ten times. Next it was heated for several hours at 140°, then for two hours at about 230° in an electric air-bath, and, after it had cooled in a desiccator, it was weighed. In order to determine how much moisture was retained by the precipitate, in each case it was transferred as completely as possible to a clean porcelain crucible and weighed; then the salt was fused by heating the small crucible, contained in a large covered crucible, and again weighed. The fused salt was light yellow as a rule, showing that no appreciable reduction had taken place. The asbestos mechanically detached from the Gooch crucible, together with a minute quantity of silver bromide which occasionally escaped the crucible, was collected from the filtrate and wash-waters upon a small filter, the ash of which was treated with nitric and hydrobromic acids before weighing. Although the filtrates and first wash-waters were essentially free from dissolved silver bromide, the subsequent wash-waters usually contained a trace of silver bromide. The amount of dissolved salt was determined with the nephelometer by comparison with standard bromide solutions.

Several difficulties were met in carrying out the analyses. In the first place it proved difficult to wash the platinum boat absolutely clean. When rinsed with cold water only, and dried at 100°, the weight was in many cases a few hundredths of a mgrm. greater than before fusion of the bromide. Ignition to redness of the boat thus treated then produced a slight loss in weight. Rinsing with hot water reduced the gain in weight of the boat after drying but did not wholly prevent a slight loss on ignition. The cause of the variation was not discovered, hence it seems safer in the calculations to use the weight of the boat after drying. The total variation is so slight, however, that it scarcely affects the final result.

Two other difficulties arose from the fact that when a solution of a manganous salt, even as dilute as the filtrates from analyses, is filtered through filter-paper, in spite of long-continued washing a small amount of manganese is tenaciously retained by the paper. This was discovered from the fact that the asbestos residues always contained manganese. In Analyses 31 to 33 it was found possible to eliminate the manganese completely by washing the filter finally with 5 per cent hydrobromic acid. In two cases (Analyses 29 and 30) the residues were analysed for manganese, and were found to contain 0·00023 and 0·00057 grm. of Mn_3O_4 respectively.

The average of these two quantities is, however, larger than the total residue in some cases, hence this value can not be used to correct the previous analyses. In order to determine accurately the proper correction for this error, a solution containing manganous nitrate in the proportion in which it was usually contained in the filtrate of an analysis, was passed through filter-paper, and the filters were then washed as thoroughly as possible with water. The ash of

these papers invariably contained manganese, the weights of manganic oxide in several experiments being found to be 0·00018, 0·00011, 0·00006, 0·00018, and 0·00005 grm. with an average of 0·00012 grm. This quantity was subtracted from the weight of asbestos shreds in all cases except Analyses 31 to 33, where the paper was washed with hydrobromic acid.

The residue obtained by the filtration of the manganous bromide proved to contain manganese, and to be free from detectable amounts of platinum and silica. Probably this insoluble residue consisted chiefly of oxides of manganese, although prolonged fusion in hydrobromic acid failed to reduce materially the proportion of insoluble matter. The discovery of adsorption in the case of manganous nitrate led to the suspicion that at least a portion of this residue was due to adsorption of manganese compounds by the filter-paper. In order to test this point a solution of manganous bromide, containing about 5 grms. in 200 cc., after one filtration was again filtered through a second filter about 3 cm. in diameter. Filters of this size were used in filtering the manganous bromide solution in the analyses. This filter was then washed with water as thoroughly as in an analysis, and was ignited. The weight of manganic oxide obtained was 0·00008 grm. Two repetitions of the experiment yielded 0·00008 and 0·00010 grm. respectively. If, as is probable, the manganese is adsorbed, not as bromide, but as some basic compound, possibly as manganic hydroxide, the bromine would have remained partially, if not wholly, in the solution. In that case a suitable correction could be applied by subtracting from the weight of the residue the average of the quantities of manganese adsorbed in the above experiments. An attempt to prevent the difficulty by adding dilute sulphuric acid to the solution of manganous bromide did not diminish the extent of the adsorption. Hence a negative correction of 0·00009 grm. is applied to the residues in all cases.

(To be continued).

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 101).

Procedures and Notes.

Procedure 1.—If the substance is a solid, note its colour, odour, and texture; examine it with a lens to determine whether it appears to be heterogeneous, and, if so, note the appearance of its constituents. Note especially whether it is an alloy or a non-metallic substance. If the substance is an alloy, pass to P. 3. If the substance is not an alloy, to determine whether organic matter or water is present in it, heat gently at first, then strongly, about 0·1 grm. of the finely powdered substance in a hard glass tube (of about 0·6 cm. bore and 8 cm. length) closed at one end. Note whether the substance blackens, whether a tarry or aqueous deposit forms on the cold part of the tube, and whether a burnt odour is emitted. If organic matter is thus proved to be absent, pass to P. 3; if proved to be present, pass to P. 2.

If the substance is a solution in water or other volatile liquid, note its odour, test it with litmus paper, and evaporate just to dryness enough to yield a residue of about 1 grm. Test a small quantity of this residue as described in the preceding paragraph. Treat the remainder by P. 3 if organic matter is found to be absent; otherwise by P. 2.

Notes.

1. When a complete analysis in the wet way is to be made, it is usually not worth while to make a more extended preliminary examination in the dry way. The closed-tube test is, however, essential, in order to show whether organic matter or water is present; and incidentally it often furnishes other valuable information.

2. Certain kinds of organic matter, especially sugars and hydroxy acids, such as tartaric, citric, and lactic acids, prevent the precipitation of the hydroxides of aluminium and chromium in the subsequent analysis, and must therefore be detected and removed. Moreover, a large quantity of organic matter of any kind interferes with the execution of the analysis; for example, with the operations of solution, filtration, and evaporation. Alloys do not contain organic matter or water; and therefore the closed-tube test need not be applied to them.

3. The closed-tube test is a more satisfactory method of detecting organic matter than heating in an open vessel. Blackening, unless accompanied by a burnt odour or by the formation of a tarry deposit, is not due to organic matter. Copper, cobalt, and nickel salts may cause it, owing to the formation of the black oxides on heating.

4. It is usually desirable to determine whether water is a constituent of the substance, and, if so, whether it is present in large or small proportion. This can be done with a fair degree of delicacy by the closed-tube test, provided care be taken to keep the upper part of the tube cool during the first of the heating. Water may be present as so-called water of constitution, as in FeO_3H_3 or Na_2HPO_4; as water of crystallisation, as in $MgSO_4.7H_2O$; as enclosed water, as in some hydrated silicates like the zeolites, or as mother-liquor within crystals; and as hygroscopic moisture on the surface. Water of constitution may be expelled only at a fairly high temperature, while in the other forms it is seldom retained above 200°.

5. The closed-tube test may also furnish evidence of the presence of certain metallic and non-metallic elements when the yare present in considerable quantity. Thus all ammonium salts and mercury compounds are volatilised much below a red heat: the former give on the upper part of the tube a white sublimate; the chlorides of mercury also give a white sublimate; while most other mercury compounds give a grey one, consisting of minute globules of mercury, made visible by a lens or by rubbing with a wire. Uncombined As, As_2O_3, and As_2S_3 are also readily volatilised, forming black, white, and yellow sublimates respectively. Of the acid-forming elements or groups, free sulphur or a persulphide is shown by a sublimate of reddish brown drops, changing to a yellow solid on cooling, and accompanied by odour of SO_2; a moist sulphide, by the odour of H_2S; a nitrate or nitrite, by brown vapours of NO_2; free iodine or a decomposable iodide, by a black sublimate of I_2 and by its violet vapour; a sulphite, by the odour of SO_2; a peroxide, chlorate, or nitrate, by evolution of oxygen, recognised by its inflaming a glowing wood-splinter held in the tube; and a carbonate or oxalate, by the evolution of CO_2, recognised by its causing turbidity in a drop of $Ba(OH)_2$ solution.

6. If the substance to be analysed is a liquid, it is desirable to determine first how much, if any, solid substance is present in it; for enough must be taken for analysis to enable small quantities of the metallic elements to be detected. Moreover, if it is dissolved in a volatile organic solvent the latter is removed by evaporation.

Procedure 2.—If the closed-tube test (P. 1) has shown the presence of organic matter, powder, or cut into small pieces, 1 to 5 grms. of the substance (according to the quantity of organic matter present). Add to it in a casserole about 5 cc. H_2SO_4 (1·84); warm gently until the substance is well charred; cool; add slowly, with constant stirring under a hood, HNO_3 (1·42) until violent reaction ceases; digest for a few minutes on a steam bath,

* From the *Technology Quarterly*, xix., No. 3, September, 1906.

and then heat over a flame, keeping the dish moving, until the substance is thoroughly charred. Cool, again add HNO_3 as before, and heat until thick fumes of H_2SO_4 are evolved; cool somewhat, and add a little HNO_3. Repeat this process till the H_2SO_4 becomes light coloured and remains so when heated strongly.

Evaporate the remaining H_2SO_4 under a hood to about 1·5 cc. Cool and add carefully about 10 cc. water. If there is a residue, cover the casserole and boil the mixture (to extract slowly dissolving sulphates); cool, filter, and wash, first with H_2SO_4 (1·20) and then with a little water, rejecting the washings. (Residue, P. 5.) To the solution add a drop of HCl (1·12). (If a precipitate forms, add more HCl, but only as long as a precipitate continues to separate; filter, wash the precipitate, and test it for silver by P. 15). Dilute the solution to a volume of 40 cc. (Solution, P. 21).

Notes.

1. This method of destroying organic matter is of very general application, being effective even when such stable substances as paraffin are present. Organic matter can also be destroyed by ignition, but this has the disadvantages of volatilising certain elements, especially mercury and arsenic, and of making some substances very difficultly soluble. When the organic matter consists only of oil, as is the case with an oil paint, it may be better to extract it with ether, especially when it is desired to determine the proximate constituents of the substance.

2. The residue contains: any substances originally present that have not been attacked by HNO_3 or H_2SO_4, especially silicates; all the lead, strontium, and barium that may have been present in any form, since the sulphates of these elements are insoluble in dilute H_2SO_4; all the silica, since silicic acid is dehydrated and made insoluble by heating with H_2SO_4; some of the calcium, bismuth, antimony, and tin, when these elements are present in moderate quantity, since their sulphates (or oxides) are not readily soluble in dilute H_2SO_4; and substantially all of the chromium, since its sulphate is converted into the insoluble anhydrous form.

3. After the organic matter is destroyed, the solution is evaporated to about 1·5 cc. and the solution is finally diluted to 40 cc., in order that the concentration of the acid may be right for the subsequent H_2S precipitation.

(To be continued).

Combination of Carbon with Nitrogen in the Elementary State.—M. Berthelot.—Pure carbon, free from hydrogen, and containing no trace of the metals of the alkalis or the alkaline earths, does not combine directly with nitrogen to form the nitride of carbon, *i.e.*, cyanogen, under the influence of heat alone at any known temperature; neither the electric current nor the voltaic arc effects the combination between the elements. The specific odour and the traces of cyanides found in gases containing nitrogen when traversed by the arc current are due the impurities which are capable of forming acetylene—a gas which combines directly with free nitrogen by means of electricity to form hydrocyanic acid. It is difficult to obtain absolutely pure carbon; the experiments on the combination of carbon with nitrogen are best carried out with the diamond, or with purified graphite, and with nitrogen absolutely dry and contained in a vessel closed so as to exclude the entrance of hydrogen. An inverse method may be employed, starting with pure cyanogen and decomposing it by means of a series of electric sparks. The author found, by continuing this process for several hours and obtaining an abundant deposit of carbon, that there was no reaction between it and the pure nitrogen when all traces of other products had been removed.—*Comptes Rendue*, cxliv., No. 7.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 21st, 1907.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MESSRS. T. S. Patterson and E. G. Streimer were formally admitted Fellows of the Society.

The PRESIDENT announced that the Society had incurred a further loss by the death of Professor Henri Moissan, which occurred on February 20th, in Paris; the late Professor Moissan was elected an Honorary and Foreign Fellow Member of the Society on January 20th, 1898.

On behalf of the Executive Committee of the Coal Tar Colour Jubilee Celebration, it was stated by the Chairman, Prof. R. Meldola, that the Council of the Society had that afternoon accepted the marble bust of Sir William Perkin, which was to be placed in the rooms of the Chemical Society according to the decision of the public meeting at which the celebration was inaugurated.

It was further stated that the Council had received and acknowledged, in the name of the Society, an important addition to the Research Fund in the form of a contribution of £1000 from the Worshipful Company of Goldsmiths.

Certificates were read for the first time in favour of Messrs. William Robert Ball, B.Sc., 48, Cambridge Road, Thornaby-on-Tees; Alexander Thomas Cameron, M.A., B.Sc., Burtonhill, Malmesbury; Geoffrey Dodleston Hope, B.Sc., Ph.D., Heath Heys, Oxton; The Hon. Raymond Egerton Hubbard, Addington Manor, Winslow; Herbert Brooke Perven Humphries, B.Sc., 117, Avenell Road, Highbury, N.; James McConnan, M.Sc., Ph.D., Danehurst, Greenbank Drive, Liverpool; Percy Joseph Rhodes, Bridge House, Church; Sydney William Smith, B.Sc., 76, Norroy Road, Putney, S.W.; Nicholas Tarr, Lucton School, Herefordshire; William Scott Tebb, M.A., M.D., Sandfield, Putney Heath Lane, S.W.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As President—Sir William Ramsay, K.C.B., F.R.S.; *vice*, Prof. R. Meldola, F.R.S.

As Foreign Secretary—Dr. Horace T. Brown, F.R.S.; *vice*, Sir W. Ramsay.

As Vice-Presidents—Prof. J. J. Dobbie, F.R.S., and Sir Alexander Pedler, F.R.S.; *vice*, Dr. H. T. Brown, F.R.S., and Prof. H. B. Dixon, F.R.S.

As Ordinary Members of Council—Mr. G. T. Beilby, Dr. W. R. Hodgkinson, Mr. E. Grant Hooper, and Dr. H. R. Le Sueur; *vice*, Prof. W. Gowland, Mr. A. D. Hall, Dr. A. Lapworth, and Mr. J. E. Marsh, F.R.S.

Mr. E. Grant Hooper, Dr. H. F. Morley, and Dr. H. R. Le Sueur were elected Auditors to audit the Society's accounts.

A ballot for the election of Fellows was held, and the following were declared duly elected:—Alfred Frederick Allen, B.Sc.; George Bagley; Frank Baker, B.Sc; Henry Bassett, jun., B.Sc., Ph.D.; Frank Stanley Benton; Leslie Hamilton Berry, B.Sc.; John Trevor Cart, B.Sc.; John Christie, B.A.; George William Clough, B.Sc.; Taylor Cook; Colin Ernest Dall, B.Sc.; Francis Davidson; William Smith Denham, B.Sc.; Mohan Nath Kedarnath Dikshit; Frederick Alldis Eastaugh; John Edwin Farmer; George Fowles; Edward William Lanchester Foxell, B.Sc.; Percival John Fryer; William Howieson Gibson, B.Sc.; William Godden, B.Sc.; William Heber Green, D.Sc.; Christopher Maurice Walter Grieb, B.Sc.; Richard Higham; William Marrs Hooton, M.A., M.Sc.; William James Hoyten, M.R.C.S., F.R.C.P.; Francis Townshend Cunynghame Hughes; Arthur Vivian Hussey; Ernest Wilfrid Jackson; Victor George Jackson; Sidney James

Jennings, B.Sc.; Albert Theodore King, B.Sc.; George Lunan; Joseph Martin, B.Sc.; Charles Pask Matthews, B.Sc.; Louis Murgatroyd; Otto Oberländer, Ph.D.; Frederic George Percy Remfry, B.A., D.Sc; Robert Robertson, M.A., D.Sc.; Arthur Henry Salway, Ph.D., B.Sc.; Charles Schlienger, B.Sc.; William George Sewell, B.Sc.; Frederick George Shepheard, B.Sc.; Robert Low Smith; William Sandilands Templeton, M.A., B.Sc.; Richard Noel Garrod Thomas, B.A.; Maximilian Toch; William George Twiney, B.Sc.; Charles Rowlatt Watkins, B.A.; Robert Burt Wight, M.A., B.Sc.; William Henry Williams; Mark Arthur Wolff.

The Council has ordered the following Report to be printed in the *Proceedings* of the Society:—

Recommendations as to the Nomenclature of the Proteins.

It is well known that much confusion arises at the present time from the lack of any understanding, either here or abroad, as to the exact sense in which the various names applied to proteins (Proteinstoffe, Eiweisskorper, Albuminoids) and their derivatives shall be used. No little difficulty is created by the use of a term in different senses, as well as ambiguity of meaning in some cases. It appeared desirable, therefore, to lay down rules for the guidance of students and workers, at all events in this country, which would tend to promote some degree of uniformity of usage. It was obviously desirable to retain existing terms as far as possible, especially as it was clear that the time has not yet come to coin strictly systematic names, and that only provisional recommendations are desirable in the existing state of knowledge.

The following Report is the outcome of a prolonged consideration of the subject by a number of chemists and physiologists. The original Committee was called into being by the Physiological Society; its members were nominated by the two societies. The Report of the Committee was subjected to criticism, both by the Physiological Society and by the Publication Committee of the Chemical Society. At the instance of the latter body a number of chemists specially interested in the subject then took the matter into consideration in conjunction with a few representatives of the Physiological Society; finally, a draft Report embodying the conclusions arrived at was prepared by Drs. Halliburton and Hopkins, which was considered and amended at a meeting of the Publication Committee of the Chemical Society, at which the physiologists were present.

Recommendations.

I. The word Proteid—which is used in different senses in this country and in Germany—should be abolished.

II. The word Protein is recommended as the general name of the whole group of substances under consideration. It is at present so used both in America and Germany. It admits readily of the use of such derived words as protease and proteose. If used at all, the term Albuminoid should be regarded as a synonym of protein.

III. The sub-classes should be as follows:—

1. *Protamines.*—These are simple members of the group. They are exemplified by substances like salmine and sturine which have been separated from fish-sperm.

2. *Histones.*—These are more complex substances; this and the previous class probably pass gradually into one another. The class is exemplified by the histones separated by Kossel from blood corpuscles; precipitability by ammonia is one of their distinguishing features.

3. *Albumins.*—These are proteins of which egg-albumin and serum-albumin may be taken as typical examples.

4. *Globulins.*—These are proteins which differ from the albumins in solubility; they are more readily "salted out" of solution than the albumins. They are exemplified by serum-globulin and fibrinogen. The class should also include certain derivatives of globulins such as fibrin and myosin.

N.B.—The carbohydrate radicle separable in small quantities from any members of Classes 3 and 4 is probably not to be considered as a prosthetic group, as it is in the gluco-proteins (see below).

N.B.—It appeared advisable, especially from the teachers' standpoint, to introduce a general term to include proteins coagulable by heat (Classes 3 and 4); but a term likely to meet with general acceptance has not yet been suggested.

5. *Sclero-proteins.* This new word takes the place of the word albuminoid in the limited sense in which the majority of physiologists have been accustomed to use it. It includes such substances as gelatin and keratin; the prefix indicates the skeletal origin and often insoluble nature of its members.

6. *Phospho-proteins.* This class includes such substances as vitellin and caseinogen with its derivative casein. The prefix nucleo frequently used in relation to this class is incorrect and misleading.

7. *Conjugated Proteins.* These are substances in which the protein molecule is united to a "prosthetic group." The principal sub-divisions are:—

a. Nucleo-proteins.
b. Gluco-proteins (*e.g.*, mucin).
c. Chromo-proteins (*e.g.*, hæmoglobin).

8. *Derivatives of Proteins.*—Of these the products of protein-hydrolysis (a term preferable to proteolysis) are those which require special attention. These should be classified as follows.

Note.—Although mindful of the unfortunate fact that terms such as proteolysis fail to convey a meaning in harmony with that which is conveyed by the terms electrolysis and hydrolysis (on which they are moulded) of decomposition *by*, the Committee have not ventured to deal with the difficulty; they recognise, however, that the practice is one to be obviated, if possible (compare Armstrong, *Proc. Roy. Soc.*, 1904, lxxiii., 500).

a. Meta-proteins.—This term is suggested in place of albuminate (acid-albumin, alkali-albumin), which is objectionable because (1) these products are obtainable from both albumins and globulins, also (2) because the termination ate implies a salt.

b. Proteoses.—This term includes albumose, globulose, gelatose, &c. The sub-division of these into proto-, hetero-, deutero-proteoses, &c., and the various modifications of Kühne's original classification have been considered; the whole subject is, however, at present too unsettled for any final nomenclature of these sub-divisions to be proposed.

c. Peptones.—This term should be restricted to the further products of hydrolysis which differ from the proteoses inasmuch as they cannot be salted out from solution, and usually resemble them in giving the biuret test.

N.B.—It has been pointed out that certain vegetable products hitherto regarded as peptones do not give the biuret test. It does not appear possible to bring such exceptional substances into any general classification at present. The same difficulty in classifying arises in connection with certain other vegetable proteins; for instance, those which like gliadin are soluble in alcohol.

d. Polypeptides.—The majority of the polypeptides are synthetical substances. Some, however, have been separated from the products of protein-hydrolysis, and it is therefore advisable to include them in the present classification. They are products of cleavage beyond the peptone stage, and consist of two or more amino-acids in association; the majority of those hitherto prepared do not give the biuret test.

IV. The term caseinogen should be used for the principal protein in milk and casein for its derivative which is the result of the action of rennet.

V. The two principal proteins of the muscle plasma should be termed paramyosinogen and myosinogen; the term soluble myosin should take the place of v. Fürth's soluble myogen-fibrin; the term myosin should be restricted to the final product formed during *rigor mortis*.

Of the following papers, those marked * were read :—

*38. "*The Constitution of Hydroxyazo-compounds.*" By WILLIAM BRADSHAW TUCK.

Several workers have proved that the ethers of all hydroxyazo-compounds and the benzoyl derivatives of the *p*-compounds possess the azo-structure, but that the benzoyl-*o*-hydroxyazo-compounds have the quinone-hydrazone configuration.

Chemical methods, however, have failed to produce a unanimous opinion with regard to the constitution of the free hydroxy-compounds.

As the absorption spectrum for azobenzene has been shown to be very different from that characteristic of quinones, several of the hydroxyazo-compounds were examined spectrographically.

The absorption spectra of the *p*-hydroxy-compounds agree extremely closely with those of their derivatives; further, hydrochloric acid produces the same very characteristic change in the spectra of the phenolic substances and their ethyl ethers. This proves that the constitution in the two cases is similar; that is, the free hydroxy-compounds are in the azo-form. The ethers of *o*-compounds also agree with the *p*-compounds, but the benzoyl derivatives are similar to benzoquinonebenzoylphenylhydrazone. The absorption spectra of all the azo-derivatives examined confirm the hypothesis previously put forward for the colour of azobenzene (*Trans.*, 1906, lxxxix., 982).

DISCUSSION.

Dr. HEWITT agreed with Mr. Tuck that in the case of the *p*-hydroxyazo-compounds, the free substances, their ethers and esters were all of the azo-phenolic type, but was uncertain whether a solution of these substances in concentrated hydrochloric acid really contained much hydrochloride, since the bases being very weak, must have suffered considerable hydrolytic dissociation.

The contention that the *o*-hydroxyazo-compounds and their benzoyl derivatives corresponded to quinone-hydrazones was based apparently on the observation of Goldschmidt and Brubacher that acyl anilides result on complete reduction of the acyl-derivatives of benzeneazo-*p*-cresol. This might, however, be equally well the result of a secondary reaction, since esters and primary amines normally react to give alcohols or phenols and acid amides. Against these equivocal results must be placed the positive evidence that on substitution these compounds behave as azophenols whether they belong to the para- or ortho-series.

The only other physical method hitherto adopted in the case of the hydroxyazo-compounds has been the application of cryoscopic determinations in non-hydroxylic solvents by Auwers and Orton, whose results indicate that the para-compounds are azophenols, and give no positive result for the ortho-substances.

Goldschmidt himself abandoned the idea that the *o*-hydroxyazo-compounds were quinone-hydrazones, and his observation that the acylated compounds of both series reduce to hydrazo-compounds which are insoluble in alkali distinctly points to acylation, with respect to oxygen, having taken place.

Dr. LOWRY said that Oddo's theory of "mesohydry" to which the author had referred was in many respects a reversion to Laar's theory of "tautomerism," since it postulated that a mobile hydrogen atom might be equally attached to oxygen and to nitrogen or carbon. If the hydrogen atom was capable under any conditions of settling in either of the alternative positions the phenomenon was not one of tautomerism, but a mere case of labile isomerism, which might become dynamic when the compound was liquefied with or without the addition of a catalyst. The separation of a single isomeride was a normal result of crystallisation, and, so far as he was aware, no gsnuine case of mesohydry or of tautomerism had yet been established. It was doubtful whether the hydrazo-compounds would prove to be an exception, although the possibility remained open that the crystals might, in certain cases, be isomorphous mixtures of two or more isomerides.

*39. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part IX. *A New General Method for Studying Intramolecular Change.*" By THOMAS STEWART PATTERSON and ANDREW MCMILLAN.

The influence of benzaa*nti*aldoxime as a solvent on the rotation of ethyl tartrate was found to be very remarkable. A method of studying intramolecular change was deseribed which had been applied in the cases of benzaldoxime, anisaldoxime, and ethyl phenylformylacetate.

*40. "*Displacement of Halogens by Hydroxyl.* I. *The Hydrolytic Decomposition of Hydrogen and Sodium Monochloroacetates by Water and by Alkali, and the Influence of Neutral Salts on the Reaction Velocities.*" By GEORGE SENTER.

By varying the initial concentration within fairly wide limits, it was shown that the hydrolytic decomposition of monochloroacetic acid by hot water according to the equation $CH_2Cl{\cdot}CO_2H + H_2O = OH{\cdot}CH_2{\cdot}CO_2H + HCl$ is strictly unimolecular up to N/2 solution; the reaction velocity is somewhat retarded by hydrochloric acid, but is not affected by sodium chloride. The conclusion is drawn that water and the undissociated acid are the reacting substances; if an intermediate compound is formed, it is the rate at which it breaks down into glycollic and hydrochloric acids which is measured.

The decomposition of sodium chloroacetate by water is strictly unimolecular in dilute solution, but in solutions more than 0·1 molar, the velocity increases more rapidly than the concentration. The reaction is retarded by neutral salts. Potassium and barium chloroacetates undergo decomposition at the same rate as the sodium salt.

The interaction of sodium chloroacetate and N/10 sodium hydroxide, according to the equation $CH_2Cl{\cdot}CO_2Na + NaOH = OH{\cdot}CH_2{\cdot}CO_2Na + NaCl$, proceeds only about ten times more rapidly than the corresponding change in aqueous solution under equivalent conditions. The reaction velocity in the presence of alkali is accelerated, and to the same extent, by such neutral salts as sodium chloride, sulphate, and nitrate in equivalent solution.

On the basis of these results and of the previous observations of Arrhenius, the hypothesis put forward by R. J. Caldwell (*Proc. Roy. Soc.*, 1906, A, lxxviii., 272), according to which the accelerating influence of neutral salts on reactions in which acids (and alkalis) exert a catalytic action is ascribed to the withdrawal of water by the salt, and consequent concentration of the reacting substances, was criticised. It is considered that the effect in question is due to the action of the ions of the salt on H′ and OH′ ions.

DISCUSSION.

Dr. SENTER, replying to Dr. E. F. Armstrong, said that in his experiments, as in those of Arrhenius quoted in the paper, the ratio of alkali and acid respectively to water was constant, except for the slight differences in the amounts of water displaced by equivalent quantities of the neutral salts employed; that these differences did not amount to more than about 1 per cent of the total volume, and were therefore negligible in comparison with the magnitude of the neutral salt effect. Moreover, it did not seem quite justifiable to conclude from the results of experiments with sucrose, the solution volume of which is large and remains unaltered on dilution, that solutions for comparison should in all cases be prepared by adding a definite weight of the solute to a definite weight or volume of the solvent (H. E. Armstrong, *Proc. Roy. Soc.*, 1906, A, lxxviii., 264); in particular, salts which in certain dilutions have a negative solution volume seem to present difficulties from this point of view.

*41. "*The Interaction of Ammonium Salts and the Constituents of the Soil.*" By Alfred Daniel Hall and Conrad Theodore Gimingham.

As it has been observed that an acid reaction develops in soil which has been repeatedly manured with ammonium salts, the authors have re-examined the action of ammonium salts on the chief constituents of soil. Solutions of various strengths, N to N 100, of ammonium sulphate, chloride, or other salt were shaken for twenty-four hours with silica, clay, calcium carbonate, and humus respectively, and the composition of the resulting solution was determined.

With silica, there is no action. With clay, a double decomposition takes place between the ammonium salt and zeolitic bodies in the clay, ammonium being withdrawn from solution and replaced by equivalent quantities of calcium, magnesium, and potassium. With varying strengths the reaction can be represented by the equation—

$$\frac{(\text{Ammonium withdrawn from solution})^x}{\text{Ammonium remaining in solution}} = K,$$

as long as the clay is in excess. If the clay is not in excess, it can only take up a fixed amount of ammonium whatever the strength of the solution. No acid reaction is produced, and there is no adsorption of the salt as a whole.

With calcium carbonate, the reaction does not proceed far, and the extent may be represented by an equation of similar form. With natural humus from various sources, the reaction is similar to that with clay; other bases, chiefly calcium, are displaced by ammonium; there is no development of acidity and no adsorption.

The acid reaction observed in the field is thus not due to inorganic causes; a biological origin has been found.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, February 22nd, 1907.

Prof. J. Perry, F.R.S., President, in the Chair.

A paper on "*Transformer Indicator Diagrams*" by Prof. T. R. Lyle was read by Prof. F. T. Trouton.

The term "transformer indicator diagram" has been applied by Professor Fleming to any series of periodic curves which give the forms, relative phase positions, and magnitudes of the waves of current and E.M.F. on both the primary and secondary sides of a transformer when working. Such diagrams have been obtained by many investigators in different ways, but by none of the methods hitherto used has it been possible to determine directly and independently either the wave of magnetic flux F in the core, or the wave of magnetising-current turns usually represented by the vector sum $n_1C_1+n_2C_2$. It is shown in the paper that the integral $\int(n_1C_1+n_2C_2)dF$ for one cycle is equal to the total iron loss per cycle, and the advantage of being able to determine both $n_1C_1+n_2C_2$ and F directly and accurately is apparent. By means of the wave-tracer designed by the author not only can the E.M.F. and current waves be accurately determined, but also the wave of magnetic flux pulsating in the core of the transformer, and in addition the magnetising current wave, $n_1C_1+n_2C_2$ can be obtained with the same accuracy as any of the other quantities. The author has already shown that if a periodic current C flows in the primary of a pair of coils whose mutual induction is M, and if the secondary be joined through a suitably arranged commutator, which commutes twice a second, to a large resistance r and thence to a galvanometer, there will be a steady deflection γ which is connected with the instantaneous value of C of the current at the instant of commutation by the relation—

$$MC = \frac{\lambda r T}{4}\gamma;$$

where λ is the reducing factor of the galvanometer and T the period. In the present paper the author uses a triad of coils, two of which (p_1 and p_2) serve as primaries and the third as a common secondary, S. If M_1 be the mutual induction between p_1 and S, and M_2 that between p_2 and S, and if the current C_1 circulates in p_1 while C_2 circulates in p_2 and the secondary S is connected through a resistance to a galvanometer, then—

$$n_1C_1+n_2C_2 = \frac{\lambda r T}{4M}\gamma;$$

where $M_1/n_1 = M_2/n_2 = M$. By suitably adjusting M_1 and and M_2, therefore, the vector sum $n_1C_1+n_2C_2$ is proportional to γ. The paper describes tests with a transformer at no load, full non-inductive load, and full inductive load. New methods of comparing mutual inductances and of measuring mutual and self-inductances are given in the paper.

Mr. W. Duddell said the paper was an interesting and important one, and congratulated the author upon the ingenious double mutual induction method by which the vector sum $(n_1C_1+n_2C_2)$ was determined electrically. In the paper the core loss was nearly constant for no load and full load, but the author had used an E.M.F. wave which was practically a sine curve. He suggested that experiments should be carried out using distorted E.M.F. waves such as occur in many generators and transformers.

Mr. A. Campbell remarked, in respect to the title of the paper, that it seemed a wanton confusion of nomenclature to use in this connection the term "indicator diagram" which had such a definite and accepted meaning in mechanics; we might as well talk of hysteresis loops as "iron indicator diagrams." Prof. Lyle's methods were interesting, particularly that for obtaining the curve of effective ampère turns $(n_1C_1+n_2C_2)$ by the use of a double mutual inductance which performed the vector addition. The author has wisely kept the mutual inductance small: without that condition the double air-core transformer might alter C_1 and C_2. It would probably be better to split it up into two separate pairs of coils. The setting of the ratio of the mutual inductances on the triple coil could be more easily done by Maxwell's null method, which was perfectly applicable to a pair of secondaries having a common primary. If various values of n_2/n_1 had to be dealt with, the two primary coils might be fixed at right angles and the secondary mounted so as to be capable of rotation with regard to the primaries in order to allow of variation in the ratio M_2/M_1. In connection with Prof. Lyle's methods of determining inductances by the help of the wave-tracer, the somewhat similar method of Dr. E. B. Rosa might be mentioned. It was interesting to see the actual hysteresis loops given; a comparison of these with ballistic tests on the same transformer would add valuable information.

Mr. A. Russell said that the author's results proved that to a first approximation the magnetising force acting on the core followed the same law and had the same amplitude at all loads. This theorem was the starting point in the ordinary engineering theory of the transformer, but this was the first time that a careful experimental proof for a particular case had been given. The magnetic leakage in the transformer experimented on must have been very small. The formula—

$$\int_t^{t+T}(n_1C_1+n_2C_2)\frac{dF}{dt}dt$$

only gave the energy absorbed per cycle when the magnetic leakage was negligibly small. In many commercial transformers it would not be safe to use this formula. The core-loss diagrams were interesting, but their value would have been greater if the transformer had been so constructed that the magnetic flux density was approximately

uniform over the cross section of the core. The internal diameter of the centre-hole iron stampings employed was only about half the external diameter, hence the magnetic flux to which the iron was subjected was almost twice as great at the inner as at the outer circumference. As the values of the permeability of the iron at these forces might vary widely, we could not tell the distribution of the magnetic flux. This prevented us from making calculations as to the hysteresis and eddy-current losses in the core. The complete solution of the transformer problem could not be obtained until we knew more about hysteresis. Apparently there were molecular "frequency changes" in the core, and any theory that would elucidate their action would be of great value to electricians. In this connection he referred to a paper read by the Chairman in 1892.

A paper by Prof. BRAGG on "*Ionisation of Gases by α-Particles of Radium*" was read by the Secretary.

The present paper contains an account of further progress in the work of determining the relative amounts of ionisation produced by the α-particle of RaC in different gases and vapours. The view is discussed that the ionisation (i) is connected with the expenditure of energy (ϵ) of the α-particle by the expression $\delta i/\delta\epsilon = kf(v)$, where k is a constant for each gas which may be termed the specific ionisation in terms of air as unity, the determination of which for various gases has been attempted in the present paper, and $f(v)$ is a function of the velocity of the α-particle only. It is established that the total number of ions produced by the α-particles of RaC varies with the nature of the gas, and is for most compound gases and vapours examined about one-third greater than for air. The conclusion is drawn that the primary action of the α-particle is a sub-atomic one. The production of ions may be considered a secondary consequence which varies with the energy expended, the speed of the particle, and the nature of the molecule ionised. The stopping-power of a gas is more nearly an additive property of the atoms in the molecule than any other property except mass, and this is an effect quite apart from the proportionality of stopping-power to the square root of the atomic weight. For atomic weights below 30 the stopping-power divided by the atomic square root is abnormally low, an effect curiously similar to the case of atomic heats. There does not appear any evidence that the chance of an atom being ionised is dependent upon whether it is already ionised, that is occasionally the molecule may lose several ions.

Mr. F. SODDY, in a letter read by the Secretary, drew attention to the parallelism between the conclusion of the author that the same molecule may become ionised more than once, and that of Rutherford that the α-particle itself is doubly charged. The view that the charge carried by the gaseous ion was the same in all classes seemed to have been definitely rendered untenable by the results of the author. So also was the view that the energy expended in the production of an ion was independent of the nature of the gas and the same in all cases. The theoretical consequences of the work of the author were of the greatest importance, for it is inconceivable that the α-particle should be able to pass through matter in the manner it has been proved to do, if the matter in question and the α-particles consisted substantially of electrons. The suggestion made finally in the paper of the relation between the ionisation and production of hydrogen and oxygen by radium had also been made independently by Rutherford.

Dr. R. S. WILLOWS said he could not agree with Mr. Soddy that the paper rendered untenable the hypothesis that all ions carried the same charge. He pointed out that the stopping-power of a gas obeyed a certain law down to atomic weights about 30, and said that this might have some relation to the fact discovered by Barkla that the secondary radiation produced by Rontgen rays followed a definite law down to atomic weights about 40.

FARADAY SOCIETY.

Ordinary Meeting, February 19th, 1907.

Dr. T. MARTIN LOWRY in the Chair.

Mr. JOHN B. C. KERSHAW, F.I.C., read a paper entitled "*The Present Position and Future Prospects of the Electrolytic Alkali and Bleach Industry.*"

The paper opens with a brief historical review. The original patent of Charles Watt for the electrolytic production of sodium or potassium hydrate and chlorine compounds was taken out fifty-five years ago; but the earliest industrial experiments were made in the early eighties, and in 1889 a 200-H.P. plant was erected at Griesheim, using the "elektron" cell, in which the diaphragms are said to be made of cement. This cell is now used extensively on the Continent, and appears to work satisfactorily and economically.

In England the earliest industrial trials were made with an asbestos diaphragm cell at Snodland in 1891-92, and afterwards with a bell type of cell. These experiments led to the formation of the Electrochemical Company at St. Helens, but the works are now closed down. The Hargreaves-Bird and the Castner cells were patented in 1892-93; the Castner-Kellner Works were started at Runcorn in 1897.

In America a Le Sueur diaphragm cell was erected in 1892 and a Castner cell at Niagara in 1897-98.

The second part of the paper contains a list of the works now operating in Europe and America, summarising, as far as information is available, power used, type of cell and process employed, and products made. The totals show that about 55,000 H.P. are now being devoted to the production of alkalis and bleach by the electrolytic method, and that plant representing about 13,000 H.P. is lying in reserve. Assuming that all the plants are being worked to the best advantage, the production of 70 per cent caustic soda at present would be about 110,000 tons per annum, with an equivalent of 231,000 tons of 35 per cent bleaching powder (2 tons of caustic and 4·2 tons of bleach per E.H.P. year).

In conclusion the future of the industry is discussed. Within the last few years the electrolytic method appears to have had a set-back. In the author's opinion the Le Blanc, electrolytic, and ammonia soda processes will continue to exist side by side. In the case of the first, alkali and bleach will be produced in diminishing quantities, but be compensated for by the sulphur derivatives which will yield the profits. The best of the electrolytic processes will gradually replace the Le Blanc method for the manufacture of chlorine products, and they will also produce metallic sodium and its derivatives. The ammonia soda process will continue to manufacture sodium carbonate and bi-carbonate, but it can never replace the other methods, until at any rate it succeeds in making chlorine products from its waste liquors.

Mr. W. POLLARD DIGBY regretted that more information was not available regarding such points of detail as anode consumption, life and efficiency of diaphragms, &c., which would be of general use to to those engaged in the smaller electrolytic industries.

Mr. JOHN RHODIN gave some interesting details regarding the early history of the electrolytic processes. He demurred from the author's statement that these were principally developed in Germany, and he attributed the failures in this country to over-capitalisation and reckless finance, and not to any lack of skill or knowledge on the scientific side. The future will largely depend on the cost of power production.

Dr. R. SELIGMAN drew attention to some omissions in the author's list of works and products.

Dr. H. BORNS, referring to the lack of information regarding diaphragms, thought that magnesite was being used successfully.

Mr. J. C. RICHARDSON also added some interesting historical information. He favoured the "bell" type of cell in which an 84 per cent efficiency was possible.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, March 4th, 1907.

Prof. C. V. Boys exhibited a Gas Calorimeter and demonstrated its working.

The following paper was read :—

"*Five Years' Experience in Measuring and Testing Producer Gas.*" By Prof. R. Threlfall, F.R.S.

The first part of the paper is devoted to a *résumé* of the principles and construction of the instruments employed in Pitot tube gas measurement. This is followed by a description of the "static" method of measuring gas density. An account is then given of the results of balancing the make and distribution of producer gas over a period of several years, this being illustrated by curves which show that an agreement within about 2 per cent can be attained in practice.

The next section of the paper is devoted to a discussion of the theory and practice of measuring pulsating streams of gas or air, such, for instance, as are produced by pumping by gas engines, or otherwise.

The subject of recording calorimeters is next dealt with, and some records are exhibited; the calorimeter construction is not described, but there is a discussion of the general principles involved in the design, and a note on the testing of calorimeters.

The fourth part of the paper is devoted to the question of the determination of sulphur in producer gas, and it is shown that the Referee's test is less suitable for this purpose than a modification of Valentine's test, which is described. The discussion of this matter covers both the determination of sulphuretted hydrogen and of total sulphur, and it is shown that it is fatal to the sulphuretted hydrogen to employ a gas meter containing water—no matter how long it may have been in action.

The fifth part of the paper deals with testing producer gas for tar, and a proposal is made for a standard method of carrying out this investigation.

The best methods hitherto proposed and practised for the determination of the volume of gas produced per ton of coal, otherwise than by the author's meters, are considered critically, and some examples are given of the results of balancing on carbon, and on ammonia.

The paper ends with a note on the determination of producer temperatures by a system of thermo-couples, which are read by a potentiometer suitably divided to read direct and fed by a very large Clark or cadmium cell.

The paper is illustrated by many drawings and photographs.

NOTICES OF BOOKS.

The Cyanide Process of Gold Extraction. By James Park. Fourth English Edition. London: Charles Griffin and Co., Ltd. 1906.

The treatment of the cyanide process of gold extraction given in this book makes it equally suitable for the use of mining students and cyanide chemists, and from it a thoroughly sound knowledge of the most modern practical methods should readily be acquired, while the theory of the process is explained particularly clearly. Illustrative laboratory experiments are described in detail, and special attention is paid to the methods of control, testing, and analysis of solutions, many typical problems and exercises being worked out. In the fourth English Edition the treatment of silicious silver ore containing more or less gold is dealt with more fully than in the earlier editions, and the Rose process for the refining of gold and impure bullion by means of air or oxygen is also discussed, and, in fact, no recent improvement or development in cyanide practice appears to have been omitted.

Handbook on Petroleum. By Captain J. H. Thomson and Sir Boverton Redwood. Second Edition. London: Charles Griffin and Co., Ltd. 1906.

This handbook is designed for the use of inspectors under the Petroleum Acts, and for those who have the handling of petroleum and its products, and of calcium carbide. The occurrence and refining of petroleum are treated in outline only, but, on the other hand, methods of testing it are thoroughly explained, and suggestions for minimising danger in storing and transporting are made, so that the officers of local authorities will find the book of real practical value. A chapter, which is full of valuable advice, is given to the construction of oil lamps and the precautions which must be observed in order that their use may be attended by no danger. The second edition contains the new Order dealing with the keeping of calcium carbide, and an amended Order in regard to the keeping of petroleum spirit for motor-cars, besides other alterations and substitutions, and in an Appendix notes are given on the Petroleum Acts. The book is one which all who are in any way connected with the petroleum industry should not fail to acquire, for it is in every way practical and trustworthy.

Annuaire pour l'An 1907, Publié par le Bureau des Longitudes. ("Year-book for 1907, Published by the Longitude Bureau"). Paris: Gauthier-Villars.

This small volume contains in a compact form, besides copious astronomical statistics, detailed tables relating to geographical and meteorological subjects, and the weights and measures and monetary systems of the most important nations are compared. No physical or chemical data are given in this year's issue, whereas next year space will be found for them, and the geographical and meteorological information will be omitted; this alternation of contents being continued in succeeding years. The issue for 1907 contains in addition to the tables some important articles; one by M. Bouquet de la Grye discusses observations of the diameter of Venus, and the same author writes an account of the Fifteenth Conference of the International Geodetical Association, while a third paper, written by M. H. Deslandres, gives a comprehensive review of recent solar researches.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 7, February 18, 1907.

Certain Catalytic Reactions effected by means of Wood-charcoal. — Georges Lemoine. — The author describes experiments analogous to those of Abbé and Senderens upon the reducing and catalytic action of amorphous carbon in the presence of alcohols. Instead of animal charcoal, he employed bakers' wood-embers raised to a red heat, which has great absorbent power for gases. Ethyl alcohol, in presence of this charcoal heated by an electric current, is converted into aldehyde and hydrogen: $CH_3—CH_2OH = CH_3—COH + H_2$. The reaction between iodic acid and oxalic acid, to give carbonic acid and iodine, is greatly accelerated in the presence of this charcoal; less by sugar-carbon, though very greatly by platinum-black.

Some Molecular Combinations of the Metallic Halides with Organic Compounds.—V. Thomas.—It is already a published fact that iodine has the power of attacking certain metals, particularly zinc, magnesium, and aluminium, in presence of liquids such as water, alcohol, and anhydrous ether. The author, in seeking a reason for this catalytic action, concludes that the explana-

tion does not lie in the property of the solvent to bring the iodine and the metal into intimate contact, since all the solvents for iodine do not bring about any reaction; and, on the other hand, a number of organic compounds of different functions are found to effect the combination. The following are found to exercise this catalytic action:—Fatty ketones, diketones, fatty nitriles. From the examples investigated, it appears that the part played by the catalyser is of a chemical nature, and the combination effected is due to the formation of an addition compound of iodine and the solvent. The existence of a combination of iodide-alcohol is very probable, and it is ascertained that acetones and nitriles combine readily with iodides. Some examples of experiments with magnesium and with aluminium to give the iodides in presence of these catalysers are added.

Research on Gold by the Wet Method in Auriferous Sands.—Albert Fournier.—The sand used by the author for a research on the gold contained in it was relatively very ferruginous, and it was necessary to avoid the solution of the gold with relatively large quantities of other metals—iron in particular—which would mask the presence of the gold. The addition of HCl and aqua regia was found in each case inefficient for extracting the gold, which, existing in the sand largely as oxides soluble in HCl, should theoretically have been thus separated, and this led to the expectation of the presence of manganese and the consequent formation of nascent chlorine as disturbing the course of events. Taking advantage of the presence of Mn, a further addition of 5 to 10 per cent MnO_2 was made and intimately mixed with the mineral matter, the mixture being then treated with pure HCl till a clear liquid was obtained. This was followed by decantation, washing with water, and warming of the mass on the water-bath to remove HCl, and finally precipitation with alcohol. The alcohol, containing such chlorides as it was capable of dissolving, was treated for hours with a continuous current of H_2S, very small quantities of metal being thus finally detected. The use of alcohol has many advantages over water, notably the precipitation of the sulphides in better agglomerated masses and the minimum deposit of sulphur. The insoluble sulphides are washed with boiling water acidified with HCl, re-dissolved in HCl, and evaporated to dryness. This process is repeated once or twice, and finally the evaporated residue is dissolved in water. This method of obtaining the precious metals is not so rich in result when applied to small quantities of mineral as the method of fusion with lead, but the advantage lies in its necessitating the estimation of a greater weight of gold, and in any case its results are more reliable.

The Reducing and Catalytic Properties of Amorphous Carbon in the presence of Alcohols.—J. B. Senderens.—The carbon employed in the author's experiments was the black animal extract, which can be obtained very nearly pure. With ethyl alcohol, the carbon caused by catalytic action a double action to take place:—(1) $CH_3.CH_2OH = CH_2 = CH_2 + H_2O$; (2) $CH_3.CH_2OH = CH_4 + HCHO$. With propyl alcohol the second effect was very slight; the gases resulting were in the following proportions:—Propylene, 87·8; carbonic oxide, 1·3; ethane, 9·5; hydrogen, 1·4 per cent. The main reaction is expressed thus:—$CH_3.CH_2.CH_2OH = CH_3.CH = CH_2 + H_2O$. These reactions take place at far lower temperatures than that at which any dissociation of the vapours of ethyl or propyl alcohol is obtained apart from the presence of carbon.

MISCELLANEOUS.

South-Western Polytechnic, Chelsea.—The Lord Alverstone, G.C.M.G., presents Prizes and Certificates to Students of Evening Classes and Day College on March 15th at 8 o'clock p.m.

Royal Institution.—On Thursday next, March 14, at 3 o'clock, Dr. C. W. Saleeby begins a course of two lectures on "Biology and Progress." The Friday Evening Discourse on March 15 will be delivered by Professor Lunge, on "Problems of Applied Chemistry"; and on March 22 by Professor J. J. Thomson, on "Rays of Positive Electricity."

MEETINGS FOR THE WEEK.

Monday, 11th.—Society of Arts, 8. (Cantor Lectures). "Romanesque Ornament," by F. Hamilton Jackson.

Tuesday, 12th.—Royal Institution, 3. "The Visual Apparatus of Man and Animals," by Prof. William Stirling.

Wednesday, 13th.—Society of Arts, 8. "Mediæval Stained Glass—its Production and Decay," by Noel Heaton.

Thursday, 14th.—Royal Institution, 3. "Biology and Progress," by Dr. C. W. Saleeby, F.R.S.E.

—— Society of Arts, 4.30. "The City of Madras," by Sir James Thomson, K.C.S.I., &c.

Friday, 15th.—Royal Institution, 9. "Problems of Applied Chemistry," by Prof. George Lunge.

Saturday, 16th.—Royal Institution, 3. "Röntgen, Cathode, and Positive Rays," by Prof. J. J. Thomson.

Erratum.—P. 104, col. 1, line 25. *Read* "By Samuel Smiles and Thomas Percy Hilditch."

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THE CHEMICAL NEWS.

Vol. XCV., No. 2468.

A COMPARISON AND CRITICISM OF THE METHODS FOR THE DETECTION AND ESTIMATION OF COCOANUT OIL IN BUTTER.

By T. R. HODGSON, B.A. (Cantab.).

1. *The Reichert-Wollny Number.*—In these experiments the usual method was followed. Five grms. were hydrolysed and afterwards the volatile acids distilled, filtered, and titrated; the insoluble fatty acids were then dissolved in alcohol and titrated. The following results were obtained:—

	Reichert-Wollny number.	Cc. N/10 NaOH required for alcoholic solution.
Pure butter fat	27·6	2·5
90 per cent butter fat and 10 per cent cocoanut oil ..	25·7	3·1
80 per cent butter fat and 20 per cent cocoanut oil ..	24·4	3·8
50 per cent butter fat and 50 per cent cocoanut oil ..	19·3	6·4
Pure cocoanut oil	9·6	14·1

As will be seen, more than 10 per cent of cocoanut oil must be added to the butter fat before the Reichert-Wollny number is brought below the standard.

The increase in the number of cc. of N/10 NaOH does not correspond with the increase in the amount of cocoanut oil present in the sample.

It has been suggested that the ratio $\frac{\text{Insoluble acids} \times 100}{\text{Soluble acids}}$ should give a number—

For pure butter fat.. .. between 10 and 15
For pure cocoanut oil .. „ 210 „ 280

The ratios, calculated on the numbers given above, are—

Pure butter fat	9·0
90 per cent butter fat and 10 per cent cocoanut oil	11·8
80 per cent butter fat and 20 per cent cocoanut oil	15·6
50 per cent butter fat and 50 per cent cocoanut oil	33·1
Pure cocoanut oil	146·8

It will be seen that there is no regular increase in the number with increase of cocoanut oil.

I am of opinion that this method is absolutely untrustworthy as a quantitative experiment, especially as it is unable to detect 10 per cent or less of added cocoanut oil.

2. *Thorpe's Method* (*Analyst*, xxxi., p. 173).—Thorpe first proceeds as in the Reichert-Wollny method. He distils off 110 cc., filters, and titrates in the usual way; he then adds 110 cc. of water to the flask and distils off another 110 cc.; he cools and pours over the same filter and titrates the second filtrate; he then washes the apparatus with 50 cc. of alcohol and pours this over the filter, and then washes the filter with another 50 cc. of alcohol (90 per cent), slightly warmed, and finally titrates the alcoholic solution with N/10 NaOH and phenolphthalein. Thorpe's numbers are:—(See Table, next column).

Thus in Thorpe's numbers there is apparently no connection—or only a very slight one—between the increase in the number of cc. of N/10 NaOH solution required and the increase in the proportion of cocoanut oil; the average increase being 2·3 cc. for every 10 per cent of cocoanut oil present.

	Reichert-Wollny number.	Cc. N/10 NaOH required for— Second filtrate.	Alcoholic solution.
Butter fat	29·2	3·1	7·6
90 per cent butter fat and 10 per cent cocoanut oil	27·1	3·7	10·2
80 butter fat and 20 cocoanut oil	24·6	4·0	15·5
70 butter fat and 30 cocoanut oil	23·4	4·0	18·1
60 butter fat and 40 cocoanut oil	21·5	3·9	20·1
50 butter fat and 50 cocoanut oil	19·4	4·2	21·8
40 butter fat and 60 cocoanut oil	17·6	4·4	24·4
30 butter fat and 70 cocoanut oil	15·1	4·2	26·0
20 butter fat and 80 cocoanut oil	13·3	4·4	27·1
10 butter fat and 90 cocoanut oil	10·6	4·4	29·1
Pure cocoanut oil ..	8·0	4·0	34·0

The objection to this method is that, just at the point where it would be most useful (that is, between 10 and 20 per cent of cocoanut oil) the constant nearly doubles itself.

My own numbers differ considerably from Thorpe's.

	Reichert-Wollny number.	Cc. N/10 NaOH required for— Second filtrate.	Alcoholic solution.
Butter fat	28·0	2·7	3·3
80 per cent butter fat and 20 per cent cocoanut oil	24·9	3·3	12·0
70 per cent butter fat and 30 per cent cocoanut oil	22·4	3·6	13·4
Pure cocoanut oil ..	9·5	4·6	27·8

The number of cc. of N/10 NaOH required for the alcoholic solution in this case shows a rise of 3·4 for every 10 per cent of cocoanut oil on the average, but there is no regular increase.

Taking the number of cc. of N/10 NaOH required for the alcoholic solutions in the author's results, in the case of the mixtures of 20 per cent cocoanut oil and 80 per cent butter fat and 30 per cent cocoanut oil and 70 per cent butter fat, and comparing them with the numbers obtained for similar mixtures by Thorpe, one is struck by the fact that they would have to be returned as containing 15 and about 20 per cent of cocoanut oil, or a loss of 5 per cent and 10 per cent of cocoanut oil respectively; or, if the factor obtained from Thorpe's results is used, they would have to be returned as containing 33 and 44 per cent of cocoanut oil respectively, or an excess of 13 per cent in the one case and 14 per cent in the other.

This method is evidently useless as a means of estimating the percentage of cocoanut oil present in the sample, unless the analyst has a sample of the original pure butter in his possession.

As a means of detection of the presence of cocoanut oil the method has a certain amount of use, inasmuch as Thorpe says that the number of cc. of N/10 NaOH required for pure butter never exceeds 8·4; and therefore if any sample requires more than 8·4 cc., it points to adulteration.

3. *Iodine Absorption Method.*—These experiments were performed with Hann's solution of iodine bromide in glacial acetic acid, as this solution requires a much shorter time for complete saturation than Hübl's solution; but, on the other hand, the numbers obtained are usually somewhat higher than those obtained with the Hübl solution, The numbers obtained were as follows:—

Pure butter fat	40·3
80 per cent butter fat and 20 per cent cocoanut oil..	35·3
70 per cent butter fat and 30 per cent cocoanut oil..	31·7
Pure cocoanut oil	8·7

This method shows a more or less regular decrease of about 3 per cent for every 10 per cent of cocoanut oil added. Taking the highest iodine value for cocoanut oil 9·5 and using the factor 3, from the above results the calculated amounts of cocoanut oil are 14 per cent and 26 per cent, or a loss of 6 per cent of cocoanut oil in the one case and 4 per cent in the other.

4. *Saponification Number.*—The usual method was followed, the saponification with N/2 alcoholic potash and titration of the excess of potash with N/2 hydrochloric acid and phenolphthalein.

The saponification number is calculated as the number of grms. of KOH required to saponify 100 grms. of the sample. The numbers obtained were:—

Pure butter fat	22·6
80 per cent butter fat and 20 per cent cocoanut oil..	23·1
70 per cent butter fat and 30 per cent cocoanut oil..	23·3
Pure cocoanut oil	23·5

The numbers approximate so closely together that the method may be dismissed as practically useless.

5. *Extraction of Cholesterol or Phytosterol* (Foster and Reichman, *Analyst*, 1897, p. 131).—Fifty grms. of the sample were boiled for five minutes under a reflux condenser with two successive portions of 75 cc. each of 95 per cent alcohol; the alcohol was separated in a tap funnel, a piece of KOH was added to the mixed alcoholic solutions, which were then evaporated to dryness; the residue was then taken up with water and extracted with ether; the ether was then evaporated, and the residue dissolved in 95 per cent alcohol and allowed to crystallise.

Cholesterol crystallises in large plates and phytosterol in needles.

The phytosterol is very difficult to crystallise, and must be allowed to do so slowly.

Since cholesterol is only present in animal fats or oils and phytosterol only in vegetable, the presence of phytosterol may be taken as a proof of the admixture of vegetable oils, and it is said that when mixtures of cholesterol and phytosterol are crystallised, even when the cholesterol is in excess by 20 to 1, the form of the crystals leans towards that of phytosterol.

6. *Wigsmann and Reijst's Method* (*Zeit. Nahr. Genussen*, 1906, xi., 267—271).—Wigsmann and Reijst suggest the following method:—Five grms. of the fat are treated in the ordinary Reichert-Meissl method, and to the neutralised distillate they add 40 cc. of N/10 $AgNO_3$ solution; the precipitate is collected on a filter and washed until the filtrate amounts to 200 cc.; 50 cc. of N/10 NaCl are then added to the latter, and the excess of chloride is titrated back with the $AgNO_3$ solution, using potassium chromate as indicator.

The number of cc. of $AgNO_3$ solution used increased by one-tenth gives the first silver number.

Another 5 grms. are then saponified and distilled, and when 100 cc. have been collected, 100 cc. of water are added to the flask and the distillation continued; the addition of water is once more repeated; the distillates (300 cc.) are mixed and 250 cc. are neutralised, 40 cc. of N/10 $AgNO_3$ solution added, the precipitate collected and washed until the filtrate amounts to 350 cc.; 50 cc. of N/10 NaCl are then added and titrated back as before.

This number of cc. + one-fifth gives the second silver number. In the case of pure butter the second silver number is equal to the first silver number, and in the case of cocoanut oil the second silver number is greater than the first silver number.

This method is an excellent qualitative test, but quantitatively it is of no value, since the increase of the second silver number over the first silver number is extremely variable and apparently bears no relation to the amount of cocoanut oil present. Taking Wigsmann's and Reijst's own numbers, the increase of the second silver number over the first silver number varies indiscriminately from 0·25 to 4·3 in the presence of 5 per cent of cocoanut oil, and from 1·4 to 4·4 in the presence of 10 per cent of cocoanut oil.

Finally, the saponification number is of no practical value, either qualitatively or quantitatively. The Reichert-Wollny number may show some indication of the presence of cocoanut oil if the amount present in the sample is large. Wigsmann and Reijst's method is by far the best qualitative experiment, since it shows a difference between the two silver numbers in the presence of even as little as 5 per cent of cocoanut oil, but as a quantitative method it is of no value.

Thorpe's method is an excellent confirmatory test, as is also the extraction of phytosterol.

The only exact quantitative method is the iodine absorption, and I believe that the results obtained by the more general use of this method would be of much greater value than those obtained with methods of high theoretical importance, but which are at the same time of little or no value to the practical analytical chemist.

PREPARATION OF TITANIUM TETRACHLORIDE FROM RUTILE.

By H. R. ELLIS, B.Sc., F.C.S.

RUTILE was heated up to 1000° C. in a muffle furnace, and whilst red-hot suddenly plunged into cold water. This treatment rendered the substance so brittle that it was easily reduced to a fine powder in an iron mortar.

The dry powder was sifted through a fine sieve and heated to about 500° C. in the front part of the muffle furnace; whilst still hot it was mixed with a little less than half its own weight of fine aluminium powder in a Hessian crucible.

In order to start the reaction, a mixture of dry TiO_2 and Al powder was spread over the top and ignited by burning magnesium. The reaction proceeds steadily, and the whole of the rutile is attacked. The contents of the crucible were covered with a layer of magnesium as soon as the action commenced; this protected the hot titanium from contact with the air.

The bodies present after the reaction consisted of iron, titanium, silicon, and alumina. As soon as the contents of the crucible had cooled somewhat, its contents were transferred to a combustion tube and heated to redness in a steady current of chlorine, which was supplied from a cylinder and was passed through one wash-bottle containing strong sulphuric acid.

The end of the combustion tube was bent downwards slightly and passed into the bulb of a Wurtz flask, the side tube of the flask was closed with a $CaCl_2$ drying-tube. The titanium tetrachloride soon began to distil into the flask, whilst the iron chloride settled on the cooler parts of the tube; with a good sample of rutile the amount of iron chloride produced is very small; if the amount of iron present is large the tube must be made wider. No aluminium chloride should be produced, excess of aluminium not being used. The crude product was purified by distillation; the first distillate, consisting chiefly of chlorine and silicon tetrachloride, amounted to about one-fifth of the whole. The second portion was collected from 120—137° C., was again distilled, and finally distilled from a very small quantity of mercury, which retained the last traces of chlorine; the pure body distilled at 136° C.

Reaction of Aluminium Powder and Silica.

Since a fairly large amount of silicon tetrachloride was produced in the above preparation, it is quite evident that

aluminium attacks silicates or silica, producing silicon. Experiments were tried with various samples of silica in order to see how readily this reduction took place.

A mixture of pure dry sand and aluminium powder (quantities in accordance with the equation $4Al + 3SiO_2 = 2Al_2O_3 + 4Si$) was first employed. This would not react in the cold, even when a layer of magnesium was ignited on the top.

When this mixture was heated to about 500° C. in the furnace and again treated with magnesium, the reduction took place slowly and needed heat to proceed to an end.

A sample of kieselguhr was mixed with aluminium powder and similarly treated; this behaved in a similar manner, and the reduction took place slowly. A mixture of magnesium powder and kieselguhr reacted with great violence. The large heat development in the formation of alumina from rutile accounts for the easy reduction of the silica and silicates present.

Chemical Laboratory,
The Polytechnic, Regent Street, W.

A REVISON OF THE ATOMIC WEIGHT OF MANGANESE.*

By GREGORY PAUL BAXTER and MURRAY ARNOLD HINES.

(Concluded from p. 113).

The Analysis of Manganous Chloride.

The apparatus employed for the fusion of manganous chloride was very similar to that used in the fusion of the bromide. Hydrochloric acid gas was generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid. The gas was freed from spray in a gas washing-bottle, and was dried in five towers filled with beads moistened with concentrated freshly boiled sulphuric acid. From the towers the gas passed into the bottling apparatus in which the salt was fused in a current of hydrochloric acid, and bottled in pure dry air as described above. This apparatus also was made wholly of glass with the exception of the air-drying powers which were closed with rubber stoppers. Since the salt was not heated in air no error could arise from this source.

In a few preliminary experiments the hydrochloric acid gas was passed finally over freshly sublimed phosphorus pentoxide, but this drying agent was subsequently eliminated since it was found to introduce volatile phosphorus compounds into the hydrochloric acid, and thus into the manganous chloride, if the latter was moist. The effect of this difficulty upon previous work in this laboratory in the case of the analysis of chlorides which were fused in a current of hydrochloric acid gas, has been discussed elsewhere, and has been shown to have been negligible (Baxter, Hines, and Frevert, *Journ. Am. Chem. Soc.*, 1906, xxviii., 779). In the same place it has also been shown that hydrochloric acid gas attacks sulphuric acid to so slight an extent that the latter may safely be used to dry the former.

Although at first sight it is to be expected that hydrobromic acid, if dried by means of phosphorus pentoxide, would act upon this substance in a way similar to the action of hydrochloric acid gas, it has been shown that no such difficulty exists if the hydrobromic acid is as dilute as in our work (*Journ. Am. Chem. Soc.*, 1906, xxviii., 781), the maximum concentration attainable by passing nitrogen through bromine at ordinary temperatures, and then over phosphorus being not greater than 30 per cent by volume.

The principal point of difference between the analyses of manganous bromide and manganous chloride was occasioned by the greater solubility of silver chloride. This introduced no difficulty in the case of the titrations, although the opalescence in both nephelometer tubes was of course more marked at the end-point. In order to make the precipitation of the silver chloride more complete, however, a much larger excess of silver nitrate was necessary than in the case of silver bromide, about fifteen hundredths of a grm. being added in each analysis. Furthermore, the precipitate was washed at first with a solution of silver nitrate containing four hundredths of a grm. in a litre, although the final six washings were performed with water. The silver chloride dissolved in both filtrate and washings was determined by comparison as previously described. Here even the filtrate showed a trace of dissolved silver chloride.

In the case of manganous chloride also the extent of the adsorption of manganese compounds by the filter-paper was investigated by filtering a solution of the salt through a filter-paper, and, after thoroughly washing the paper, determining the residue after ignition. The correction for adsorption thus found, 0·00006 grm., is in some cases larger than the weight of the residue minus the loss in weight of the boat, owing possibly to the fact that not all the platinum lost by the boat is collected upon the filter-paper. At any rate the uncertainty introduced by applying the correction wherever possible is very small.

The filter upon which the asbestos shreds were collected was washed with warm dilute hydrochloric acid to eliminate adsorbed manganese compounds, so that no correction for adsorption is here necessary. This acid was then tested for silver chloride with the nephelometer, and if any was found it was added to the main weight of this substance.

In Analyses 32, 33, 34, 35, and 38 the silver nitrate was added to the manganous chloride, while in Analyses 36 and 37 precipitation was performed in the reverse fashion.

The possibility of the existence of manganic compounds in the salts was considered. In order to determine whether or not this was the case, one specimen of manganous chloride after fusion in hydrochloric acid was tested for manganic compounds by adding a solution of starch-paste and potassium iodide. No coloration resulted even after the addition of hydrochloric acid, although a trace of permanganate produced immediate coloration in the same solution.

The fused salts were pink in the case of both the chloride and the bromide, hence Forchhammer's statement that the pink colour of manganous salts is due to the presence of manganic compounds is incorrect (*Ann. Phil.*, N.S., 1821, i., 50).

It has already been shown that chlorides and bromides which have been fused and allowed to solidify in an acid atmosphere occlude none of the gas, for they give neutral solutions (Richards, *Proc. Am. Acad.*, 1893, xxix., 59; *Journ. Am. Chem. Soc.*, 1902, xxiv., 376; Richards and Baxter, *Proc. Am. Acad.*, 1899, xxxiv., 367; Baxter and Hines, *Journ. Am. Chem. Soc.*, 1905, xxvii., 227).

The Nephelometer.—The nephelometer employed for the estimation of slight opalescences has already been described in detail by Richards and Wells (*Am. Chem. Journ.*, 1904, xxxi., 235; 1906, xxxv., 510). All the precautions necessary for the accurate use of this instrument were carefully observed. The two tubes to be compared were always of the same size. The source of light in the nephelometer was so adjusted that tubes containing exactly equal amounts of precipitate gave identical readings. It was found advantageous to insert a plate of ground glass between the source of light and the test-tubes. In making up the test solutions, great pains were taken that the concentration of electrolytes in the two solutions and the conditions of precipitation should be as nearly as possible the same. Final readings were taken only after the ratio between the two tubes had become constant.

Vacuum Corrections.—In order to find accurately the vacuum corrections for manganous bromide and chloride, it was necessary to determine the densities of these two salts. The experiments were carried out exactly as described in our determinations of the specific gravities of

* From the *Journal of the American Chemical Society*, xxviii., No. 11.

THE ATOMIC WEIGHT OF MANGANESE.

Series I.—$MnBr_2 : 2Ag$. (Ag = 107·930, Br = 79·953).

No. of analysis.	Sample of $MnBr_2$	Sample of Ag.	Wt. of $MnBr_2$ in vacuum (grms.).	Corrected weight of residue (grm.).	Change in weight of boat (grm.).	Weight of Ag in vacuum (grms.).	Weight of Ag added or subtracted (grm.).	Corrected weight of $MnBr_2$ (grms.).	Corrected weight of Ag (grms.).	Atomic weight of manganese.
1.	A_2	K	6·53738	0·00000	−0·00004	6·56772	−0·00017	6·53738	6·56755	54·962
2.	A_1	K	4·81026	0·00019	+0·00002	4·83243	−0·00005	4·81005	4·83238	54·957
3.	C_1	K	4·88124	0·00027	0·00000	4·90354	0·00000	4·88097	4·90354	54·960
4.	C_1	H	5·63234	0·00022	−0·00007	5·65833	−0·00020	5·63219	5·65813	54·964
5.	A_1	H	5·79927	0·00008	−0·00005	5·82610	−0·00010	5·79924	5·82600	54·963
6.	C_1	J	6·59033	0·00046	+0·00004	6·62051	−0·00010	6·58983	6·62041	54·957
7.	B_1	H	4·19917	0·00016	−0·00010	4·21809	+0·00030	4·19911	4·21839	54·967
8.	A_1	J	3·59834	0·00015	+0·00010	3·61478	0·00000	3·59809	3·61478	54·957
9.	B_1	J	5·16345	0·00019	−0·00008	5·18711	0·00000	5·16334	5·18711	54·965
10.	B_1	K	3·92230	0·00014	−0·00010	3·94021	+0·00021	3·92226	3·94042	54·959
11.	B_1	K	4·49181	0·00032	−0·00009	4·51220	+0·00030	4·49158	4·51250	54·953
12.	C_1	H	3·60099	0·00016	+0·00012	3·61746	−0·00010	3·60071	3·61736	54·960
13.	D_1	H	4·77414	0·00022	0·00000	4·79602	+0·00018	4·77392	4·79620	54·951
14.	D_1	J	3·57674	0·00015	−0·00001	3·59323	−0·00004	3·57660	3·59319	54·957
15.	D_2	H + J	5·69991	0·00026	−0·00007	5·72586	+0·00055	5·69972	5·72641	54·948
								Average		54·959

Series II.—$MnBr_2 : 2AgBr$. (Ag = 107·930, Br = 79·953).

No. of analysis.	Sample of $MnBr_2$	Weight of $MnBr_2$ in vacuum (grms.).	Corrected weight of residue (grm.).	Change in weight of boat (grm.).	Weight of AgBr in vacuum (grms.).	Loss on fusion (grm.).	Corrected weight of asbestos (grm.).	Weight of AgBr from wash-waters (grm.).	Corrected weight of $MnBr_2$ (grms.).	Corrected wt. of AgBr (grms.).	Atomic weight of manganese.
16.	A_2	5·58461	0·00037	+0·00008	9·76524	0·00032	0·00069		5·58416	9·76561	54·964
17.	A_2	5·63458	0·00022	+0·00004	9·85295	0·00030	0·00073	0·00007	5·63432	9·85345	54·961
18.	A_2	6·53738	0·00000	−0·00004	11·43246	0·00029	0·00078	0·00005	6·53738	11·43300	54·957
19.	A_1	4·81026	0·00019	+0·00002	8·41199	0·00024	0·00031		4·81005	8·41206	54·959
20.	C_1	4·88124	0·00027	0·00000	8·53619	0·00022	0·01039	0·00006	4·88097	8·53642	54·950
21.	C_1	5·63234	0·00022	−0·00007	9·84971	0·00009	0·00046		5·63219	9·85008	54·954
22.	C_1	6·52653	0·00017	+0·00010	11·41232	0·00018	0·00061	0·00018	6·52626	11·41293	54·968
23.	A_1	5·79927	0·00008	−0·00005	10·14153	0·00013	0·00061	0·00005	5·79924	10·14206	54·957
24.	A_1	3·59834	0·00015	+0·00010	6·29262	0·00014	0·00023		3·59809	6·29271	54·952
25.	B_1	5·16345	0·00019	−0·00008	9·02941	0·00005	0·00023	0·00004	5·16334	9·02959	54·966
26.	B_1	3·92230	0·00014	−0·00010	6·85939	0·00012	0·00012	0·00041	3·92226	6·85968	54·951
27.	B_1	4·49181	0·00032	−0·00009	7·85527	0·00015	0·00059		4·49158	7·85571	54·942
28.	C_1	3·60099	0·00016	+0·00012	6·29731	0·00014	0·00023		3·60071	6·29740	54·949
29.	D_1	4·77414	0·00022	0·00000	8·34878	0·00020	0·00057		4·77392	8·34915	54·951
30.	D_1	3·57674	0·00015	−0·00001	6·25541	0·00018	0·00046		3·57660	6·25569	54·933
31.	D_2	5·69991	0·00026	−0·00007	9·96830	0·00020	0·00030		5·69972	9·96840	54·947
								Average, rejecting Analysis 30			54·955
								Average of Series I. and II...			54·957

Series III.—$MnCl_2 : 2Ag$. (Ag = 107·930, Cl = 35·473).

No. of analysis.	Sample of $MnCl_2$	Sample of Ag.	Weight of $MnCl_2$ in vacuum (grms.).	Corrected weight of residue (grm.).	Change in weight of boat (grm.).	Weight of Ag in vacuum (grms.).	Weight of Ag added or subtracted (grm.).	Corrected wt. of $MnCl_2$ (grms.).	Corrected weight of Ag (grms.).	Atomic weight of manganese.
32.	B_2	L	4·62985	0·00017	−0·00002	7·93730	+0·00010	4·62970	7·93740	54·960
33.	B_1	L	3·52899	—	−0·00001	6·05071	−0·00030	3·52899	6·05041	54·958
34.	B_1	L	3·30881	0·00000	−0·00010	5·67299	−0·00020	3·30881	5·67279	54·960
35.	E_1	L	3·56859	0·00014	+0·00002	6·11818	0·00000	3·56843	6·11818	54·955
36.	E_1	K	3·45114	0·00023	+0·00008	5·91647	−0·00010	3·45083	5·91637	54·958
37.	B_1	L	4·47948	0·00008	−0·00015	7·68015	−0·00020	4·47948	7·67995	54·959
38.	E_1	M	3·92089	0·00002	−0·00005	6·72232	−0·00005	3·92089	6·72227	54·958
								Average		54·958

THE ATOMIC WEIGHT OF MANGANESE (*continued*).

Series IV.—$MnCl_2$: 2AgCl.

No. of analysis.	Sample of $MnCl_2$	Weight of $MnCl_2$ in vacuum (grms.).	Corrected weight of residue (grm.).	Change in weight of boat (grm.).	Weight of AgCl in vacuum (grms.).	Loss on fusion (grm.).	Weight of asbestos (grm.).	Weight of AgCl from wash waters (grm.).	Corrected wt. of $MnCl_2$ (grms.).	Corrected wt. of AgCl (grms.).	Atomic weight manganese.
39.	B_2	4·62985	0·00017	0·00002	10·54532	0·00006	0·00017	0·00098	4·62970	10·54641	54·957
40.	B_1	3·52899	—	−0·00001	8·03616	0·00013	0·00046	0·00219	3·52899	8·03868	54·962
41.	B_1	3·30881	0·00000	−0·00010	7·53598	0·00014	0·00040	0·00107	3·30881	7·53731	54·959
42.	E_1	3·56859	0·00014	+0·00002	8·12767	0·00005	0·00042	0·00128	3·56843	8·12932	54·950
43.	E_1	3·45114	0·00023	+0·00008	7·85947	0·00012	0·00053	0·00141	3·45083	7·86129	54·952
44.	B_1	4·47948	0·00008	−0·00015	10·20110	0·00007	0·00078	0·00191	4·47948	10·20372	54·963
45.	E_1	3·92089	0·00002	−0·00005	8·92964	0·00004	0·00038	0·00142	3·92089	8·93140	54·962

Average .. .. 54·958

Average of Series III. and IV. .. .. 54·958

cadmium halides (*Am. Chem. Journ.*, 1904, xxxi., 220), with the following results :—

Density of $MnBr_2$.
(Density of Toluene, 25°/4° = 0·86156).

Weight of $MnBr_2$ in vacuum.	Weight of toluene displaced in vacuum.	Density of $MnBr_2$.
Grms.	Grm.	25°/4°.
0·0098	0·5914	4·385
3·0342	0·5963	4·384

Average .. .. .. 4·385

Density of $MnCl_2$.
(Density of Toluene, 25°/4° = 0·86166).

Weight of $MnCl_2$ in vacuum.	Weight of toluene displaced in vacuum.	Density of $MnCl_2$.
Grms.	Grm.	25°/4°.
1·9436	0·5617	2·982
2·8532	0·8266	2·974
3·1202	0·9035	2·976

Average .. .. .. 2·977 (*a*)

(*a*) Shröder obtained the value 2·478. "Dichtigkeitsmessungen," Heidelberg, 1873.

All weights were reduced to the vacuum standard by applying the following corrections for each apparent grm. of substance :—

	Specific gravity.	Vacuum correction.
Weights ..	8·3	
$MnBr_2$	4·385	+0·000129
$MnCl_2$	2·977	+0·000259
AgBr	6·473	+0·000041
AgCl	5·56	+0·000071
Ag	10·50	−0·000031
Toluene ..	0·862	+0·00126

The balance was a new Troemner, No. 10, and was easily sensitive to one-fiftieth of a mgrm. with a load of less than 50 grms. The weights, which were of brass, gold-plated, were occasionally carefully standardised to hundredths of a mgrm. The corrections did not vary with time, however. All weighings were made by substitution, with tare vessels as nearly like those being weighed as possible.

The atomic weights involved in the calculations are assumed to be as follows :—Ag = 107·930 ; Br = 79·953 (Baxter, *Proc. Am. Acad.*, 1906, xlii., 201) ; Cl = 35·473 (Richards and Wells, "Publications of the Carnegie Institution," 1905, No. 28).

Series	I. $MnBr_2$: 2Ag	54·959
„	II. $MnBr_2$: 2AgBr ..	54·955
„	III. $MnCl_2$: 2Ag	54·958
„	IV. $MnCl_2$: 2AgCl ..	54·958
Average		54·958

The close agreement of the averages of the four series is conclusive evidence that no serious error, such as occlusion by the silver halides, affected the method of analysis. This is strikingly shown by the ratio between the silver used and the silver halide obtained in the same analysis.

	Ag : AgBr.
Analyses 1 and 18	57·4438
„ 2 „ 19	57·4459
„ 3 „ 20	57·4426
„ 4 „ 21	57·4425
„ 5 „ 23	57·4439
„ 8 „ 24	57·4439
„ 9 „ 25	57·4457
„ 10 „ 26	57·4432
„ 11 „ 27	57·4423
„ 12 „ 28	57·4421
„ 13 „ 29	57·4454
„ 14 „ 30	57·4387
„ 15 „ 31	57·4456
Average	57·4435
Average, rejecting Analyses 14 and 30	57·4439

The most probable value for this ratio has recently been shown to be 57·4453 (Baxter, *loc cit.*).

Richards and Wells have proved beyond question that the ratio of silver to silver chloride is as low as 75·2634 (*loc. cit.*), a value which is identical with that obtained from the analysis of manganous chloride.

	Ag : AgCl.
Analyses 32 and 39	75·2615
„ 33 „ 40	75·2662
„ 34 „ 41	75·2628
„ 35 „ 42	75·2607
„ 36 „ 43	75·2595
„ 37 „ 44	75·2662
„ 38 „ 45	75·2656
Average	75·2632

It is interesting to tabulate the analyses according to the specimens of material employed.

Average of analyses with Samples A_1 and A_2 of $MnBr_2$	54·959
Average of analyses with Sample B_1 of $MnBr_2$	54·958
Average of analyses with Sample C_1 of $MnBr_2$	54·958
Average of analyses with Samples D_1 and D_2 of $MnBr_2$	54·951 (*a*)
Average of analyses with Samples B_1 and B_2 of $MnCl_2$	54·960
Average of analyses with Sample E_1 of $MnCl_2$	54·956
Average	54·957

(*a*) Analysis 30 is rejected.

Average of analyses with Sample	H	of Ag	..	54·958
" "	J	"	..	54·961
" "	K	"	..	54·959
" "	L	"	..	54·959
" "	M	"	..	54·958
Average..	..	..	..	54·959

The purification of sample B was exceptionally thorough. In the first place potassium permanganate is isomorphous with a comparatively limited number of substances, so that the initial purification by a large number of crystallisations of this substance may be expected to have eliminated every trace of impurity of heavy metals. In the second place, the final product had been many times re-crystallised in the form of two other compounds of manganese. It is almost inconceivable that any impurity could have eluded this large number of crystallisations in three different forms. That such a prolonged purification was unnecessary is shown by the agreement of the results from the other samples with that from Sample B. Even in the case of Samples A, C, D, and E the final product had been re-crystallised in at least two forms. The slightly lower results in the case of Sample D differ from the others by an amount no greater than the possible experimental error, and can not be considered to indicate that the composition of this sample is different from that of the others.

The various samples of silver also yielded essentially the same result, which confirms the statement as to the identity of the different samples made on page 111.

There can be little doubt that the final average of all four series, 54·96, represents with accuracy the relation of the atomic weight of manganese to that of silver 107·930. This value is in such close agreement with the value derived from previous investigations, that until the relation of oxygen to silver is more accurately known no change in the atomic weight of manganese need be made from the value 55·0, now accepted by the International Committee on Atomic Weights.

The main results of this research may be briefly summarised as follows:—

1. The atomic weight of manganese, referred to silver 107·930, is found to be 54·96, by analysis of both manganous bromide and manganous chloride.

2. The specific gravity of manganous bromide at 25°, referred to water at 4°, is found to be 4·385, and that of manganous chloride under the same conditions is found to be 2·977.

We are deeply indebted to the Carnegie Institution of Washington for funds which have made this investigation possible, and also to Dr. Wolcott Gibbs and the Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 114).

Procedures and Notes (continued).

Procedure 3.—If organic matter is absent (P. 1), reduce the substance to a finely divided form (as described in N. 1); weigh out into a casserole about 1 grm. if it is a non-metallic substance, or about 0·5 grm. if it is an alloy.

In case the substance is not an alloy, add to it 10 to 30 cc. water, heat to boiling, and test the solution with litmus-paper. If the substance has dissolved completely and the solution is neutral or acid, treat the solution by P. 11. If there is a residue or if the solution is alkaline, add carefully without filtering 5 to 10 cc. HNO_3 (1·42), and evaporate just to dryness.

In case the substance is an alloy, pour over it 10 cc. HNO_3 (1·20), cover the dish with a watch-glass, heat the mixture on a steam-bath as long as any action continues, adding a little HNO_3 (1·42) if action is renewed thereby, or a little water if crystalline salts have separated, and then evaporate just to dryness.

Heat the residue obtained in either case at 120—130° until it is perfectly dry, by keeping the casserole in motion over a flame, or, better, by heating it in a hot closet at that temperature for at least half-an-hour. Loosen the dehydrated residue from the dish, and rub it to a fine powder with a pestle; add to it 5 to 10 cc. HNO_3 (1·20), cover the dish, and heat on a steam-bath for ten minutes. Dilute with 20 cc. water, heat to boiling, filter, and wash the residue. (Residue, P. 4). To the solution add 5 cc. HCl (1·20) to precipitate the silver group, filter, and wash the precipitate with a little cold water, adding the washings to the filtrate. (Precipitate, P. 12; filtrate, P. 4, second paragraph).

Notes.

1. In order that in the following procedures difficultly soluble substances may be dissolved, the substance must be reduced to a very fine powder. This is usually best accomplished by grinding the substance, in small quantities at a time, in a mortar. With hard substances, and in general with minerals, an agate mortar should be used. Most alloys cannot be powdered in this way; these may be converted into a form that offers a large surface by hammering in a steel mortar, filing with a fine steel file, shaving with a knife, or converting into turnings with a lathe.

2. The quantity of the substance taken for analysis should always be approximately known; for a good qualitative analysis should show, not merely the presence or absence of the various elements in the substance, but should enable their relative quantities to be estimated. Since 1 to 2 mgrms. of almost any element can be detected by this system of analysis, the presence of 0·1 to 0·2 per cent of an element will be detected when a grm. of substance is taken, and this degree of delicacy is ordinarily sufficient. If much more than this quantity is taken, the precipitates may be so large that much time is consumed in filtering and washing them. For this reason it is best to use only about half a grm. of an alloy, since, owing to the absence of acid radicals, the same quantity of metallic elements is contained in a less amount of substance.

3. When the substance dissolves only partly in water, it is not worth while to filter off the residue and analyse it and the solution separately, unless special information in regard to the soluble constituents is desired. If therefore it is known to be partly insoluble in water, it is best treated at once with HNO_3, as is directed in the case of an alloy. If, however, it is completely soluble in water, the addition of HNO_3 is avoided, since it would have to be removed before the subsequent precipitation with H_2S.

4. If the aqueous solution has an alkaline reaction, the addition of an acid may cause precipitation of any substance held in solution by an alkaline solvent; for example, sulphur or sulphides of the tin group from an alkaline sulphide solution; silver chloride or cyanide from a potassium cyanide solution; silicic acid from sodium silicate solution; or metallic hydroxides from solutions in alkalis. An alkaline solution should therefore not be treated directly with HCl by P. 11, for the precipitate formed might contain other substances than chlorides of the silver group.

5. An acid reaction of the aqueous solution is due to hydrogen ions, which may arise from free acid, from an acid salt of a strong acid, or (by hydrolysis) from a neutral salt of a strong acid and a weak base. An alkaline reaction is due to hydroxide ions, which may arise from a soluble hydroxide, or (by hydrolysis) from a carbonate, sulphide, phosphate, borate, cyanide, or a salt of some other weak acid. It is to be noted that the

* From the *Technology Quarterly*, xix., No. 3, September, 1906.

terms "acid salt" and "neutral salt" refer only to the extent of the replacement of the hydrogen of the acid by the metallic element, and do not show the reaction towards litmus or other indicators. This reaction depends on the presence of a sufficient concentration of hydrogen or hydroxide ions to affect the indicator employed. Thus the neutral salts Na_2CO_3, Na_2S, &c., and even the acid salts $NaHCO_3$, Na_2HPO_4, react alkaline with litmus; while some other neutral salts, such as $Al(NO_3)_3$, react acid.

6. When an acid is added to a non-metallic substance or its aqueous solution, the evolution of any gas and its odour should be noted, since this indicates the nature of the acid radical present. Thus carbonates evolve CO_2; sulphides, H_2S; sulphites, SO_2; and cyanides, HCN. On boiling the HNO_3 solution, the presence of sulphides is further indicated by the separation of sulphur as a spongy or pasty mass, which floats on the surface, and may be removed by means of a spatula or rod, and the presence of iodides is shown by the liberation of free iodine, which may separate as a black precipitate, which imparts a brown colour to the solution, and which gives rise to violet vapours above it.

7. In dissolving non-metallic substances either HNO_3 or HCl may be first used, each having advantages and disadvantages of its own. HNO_3 dissolves owing to its oxidising power, many alloys and sulphides not attacked by HCl, but fails to dissolve certain oxides, especially MnO_2, Sb_2O_5, and hydrated SnO_2, which dissolve in HCl. HCl may cause the precipitation of chlorides of the silver group; while strong HNO_3 on heating oxidises sulphides partially to sulphates, and may cause the precipitation of lead, barium, strontium, and calcium sulphates; thus in either case making it sometimes impossible to determine whether complete decomposition has resulted. HNO_3 oxidises mercurous, arsenous, antimonous, stannous, and ferrous compounds to the higher state of oxidation; consequently, almost all the antimony and tin will usually be found in the residue insoluble in dilute HNO_3 after evaporation, all the mercury will be in the H_2S precipitate, and sulphur will always be precipitated by H_2S when iron is present. When HCl is used as a solvent, mercury, selenium, and arsenic in the arsenous form would be wholly or partly lost, owing to the volatility of their chlorides, in the subsequent evaporation, which is necessary in order to remove silica. For this last reason, and for the reason that the procedure is a more general one in that it provides for the solution of alloys and of a larger proportion of non-metallic substances and for the isolation of the silver group, the use of HNO_3 is here recommended. In special cases it is advantageous to use dilute HCl instead of HNO_3, especially when the substance dissolves completely in HCl, and it is not necessary to evaporate the solution to remove silica.

8. When a silicate is decomposed by acid, silicic acid may separate as a gelatinous precipitate, but even then a part of it always remains in solution, mainly as a colloid. When thoroughly dried at 100—130°, it is partially dehydrated, and becomes entirely insoluble. The HNO_3 acid solution is therefore evaporated to dryness, and the residue is heated at 120—130°, in order to remove the silica at this point; for, if it were not removed, it would appear as a gelatinous precipitate at some later stage of the analysis; thus, if it did not separate earlier, it would be precipitated by NH_4OH together with the iron group, and might then be mistaken for aluminium hydroxide. In the case of non-metallic substances which cannot contain silica, the evaporation and heating at 120—130° may be omitted.

9. With reference to the treatment of alloys with HNO_3 the following facts should be borne in mind. All the more common elements are dissolved by strong HNO_3 except antimony, tin, and silicon. These are oxidised to antimonic acid ($Sb_2O_5.nH_2O$), metastannic acid (nH_2SnO_3), and silicic acid, which separate at once as white amorphous precipitates except when only small amounts of these elements are present. Certain nitrates, especially that of lead, may separate in crystalline form from the strong HNO_3, but these dissolve upon adding water and heating to boiling. Of the more important rarer elements, titanium and tungsten, like antimony and tin, separate in the form of insoluble hydroxides; in the case of tungsten, tungstic acid (H_2WO_4) separates as a dense precipitate of a yellow colour.

10. In the case of an alloy the evaporation to dryness and heating at 120—130 serve to partially dehydrate the hydroxides of silicon, tin, antimony, titanium, and tungsten, whereby they are rendered nearly insoluble in HNO_3, and thus make possible a conclusion in regard to their presence or absence. If after having thoroughly dried the mixture at this temperature there is no residue insoluble in the HNO_3 (1·20), it shows the absence of silicon, tin, and tungsten in quantity as large as 1 mgrm., and that of antimony and titanium in quantity as large as 2 or 3 mgrms. The fact must not be overlooked, however, that in the dehydrated form even a very small residue or slight turbidity may correspond to an appreciable quantity of one of these elements. Therefore, if no residue can be seen, rub the sides of the dish gently with the rubber-covered end of a glass rod, pour into a small flask, allow the liquid to stand two or three minutes, and note whether there is any residue whatever. The knowledge that tin is absent is helpful, since the subsequent procedures for the detection of this element may be omitted. The subsequent procedures for antimony may, in the absence of a residue, also be omitted, provided quantities as small as 3 mgrms. are not to be tested for. In addition to the hydroxides named above the residue may also contain a considerable quantity of stannic phosphate or arsenate when tin and phosphorus or arsenic are simultaneously present, or of bismuth hydroxide when both antimony and bismuth are present; also small quantities of various other elements enclosed in a residue consisting of those already mentioned.

11. The hydroxides referred to in the last two notes usually separate also in the treatment of non-metallic substances with HNO_3 when the corresponding elements are present; but the non-existence of a residue must not, except in the case of silicon, be regarded as conclusive evidence of their absence in such substances. For acid radicals may be present which by combination with the hydroxides cause them to remain in solution; thus the presence of chloride or sulphate might cause a considerable quantity of tin, antimony, or titanium to dissolve, while that of phosphate might lead to the solution of even a large quantity of tungsten.

12. A black or metallic residue insoluble in HNO_3, obtained in the case of an alloy, may contain carbon or carbides, certain alloys of iron, such as ferrochrome or ferrosilicon, gold, or any of the platinum metals. If there is no such residue, it shows the absence of gold and platinum.

13. If the substance is non-metallic, the residue insoluble in HNO_3 probably consists of one or more of the following substances:—The partially dehydrated hydroxides of tin, antimony, silicon, titanium, and tungsten; the native or ignited oxides of the same elements, of aluminium, and of chromium; anhydrous chromic salts; the peroxides of manganese and lead; the sulphates of barium, strontium, and lead; the sulphides of mercury and molybdenum; silica; the silicates and fluosilicates of many elements; fluoride of calcium; the halides of silver and lead; the phosphates of tin and of rare earths; ferrocyanide of iron; sulphur; carbon; silicon carbide.

14. In regard to the precipitation of the silver group by HCl, see notes on P. 11.

Procedure 4.—To the residue insoluble in HNO_3 (P. 3) in a casserole add gradually 5 to 10 cc. HCl (1·20), and heat as long as action continues, adding more acid if necessary. If the substance does not dissolve completely in HCl, add to the mixture without filtering one-third its volume of HNO_3 (1·42), and heat gently as long as action continues, adding more of the acids if necessary.

To this solution in HCl alone, or in HCl and HNO_3, without filtering off any residue, add the filtrate obtained in P. 3, and evaporate the mixture nearly to dryness. In order to expel the HNO_3, moisten the residue with 2 to 5 cc. HCl (1·20), and evaporate to dryness. Thoroughly dry the residue by heating it at 120—130° in a hot closet or by keeping it in motion over a small flame. Add to the residue 4 cc. HCl (1·12), measured in a small graduate, and about 20 cc. water; boil gently for a few minutes if there is a residue; filter, and wash the residue thoroughly with boiling water. Pour the filtrate into a graduate, and add enough water to make its volume 40 cc. (Residue, if non-metallic, P. 5, if metallic, P. 4, N. 2; solution, P. 21).

Notes.

1. Of the substances that may be present in the residue undissolved by HNO_3 (see P. 3, N. 12 and 13) the peroxides of manganese and lead are reduced and dissolved by concentrated HCl; antimonic acid, stannic phosphate, and much metastannic acid are also dissolved by it. Upon the addition of HNO_3, whereby the strongly oxidising mixture known as aqua regia is produced, gold, platinum, and mercuric sulphide are entirely dissolved; and silver compounds, such as AgBr, AgI, and AgCN, are converted into AgCl. The chloride of silver and the sulphates of strontium and lead dissolve in large quantity in the concentrated acids, but only in much smaller quantity in the small amount of dilute HCl added after the evaporation. Some of the other substances that may be in the residue, especially the oxides and certain silicates, are slowly attacked by the strong acids, but the solvent action is not rapid enough to make this a practicable method.

2. If the original substance was an alloy, a residue after the treatment with HCl and HNO_3 probably consists, if non-metallic, only of metastannic, silicic, titanic, or tungstic acid; if black or metallic, of carbon, a platinum metal, or an alloy of iron with chromium, silicon, &c. If non-metallic, it is treated with H_2SO_4 and HF by the regular procedure, in order to test for and remove silica and to dissolve metastannic and titanic acids. If metallic, such a treatment would not effect solution; the residue is then best fused with Na_2O_2 in a nickel crucible, the mass treated with water and HCl, and the solution analysed as usual, except that nickel cannot be tested for. (For a description of this process and the results attained by it, see A. A. Noyes, "System of Qualitative Analysis including nearly all the Metallic Elements," Part I., Procedure 13, published in the *Technology Quarterly*, 1903, xvi., p. 113; see also Chemical News, xciii., p. 134 *et seq.*).

3. The solution is evaporated to render insoluble silicic acid which may have come from the decomposition of silicates, and to remove the large quantity of acid which would otherwise interfere with the H_2S precipitation. The evaporation with HCl serves, moreover, to remove HNO_3, which, if present in large quantity, would destroy the H_2S with liberation of sulphur. Since the success of the separation by H_2S of the copper and tin groups from the iron group requires a proper concentration of acid in the solution, a measured quantity of HCl is added, and the solution is diluted to a definite volume.

4. If the original substance was an alloy and a large non-metallic residue remains after treatment with HNO_3 (P. 3), it is sometimes advantageous to analyse the residue separately by the following procedure, by which a large quantity of metastannic acid is more readily dissolved:—Add to the residue in a casserole 3 to 4 cc. concentrated H_2SO_4, and heat under the hood until the acid has evaporated to a volume of about 2 cc. Cool, add an equal volume of water, cool again, add 5 cc. HCl (1·12) to dissolve antimonic oxide, and heat to boiling. Cool completely, filter if there is a residue (which may consist of silicic or tungstic acid), and add the acid solution drop by drop, with constant shaking, to a mixture of 10 cc. ammonium monosulphide, 1 cc. ammonium polysulphide, and 10 cc. NH_4OH (0·90) in a flask. Cover the flask, and digest for a few minutes on a steam-bath. Filter out the precipitate, which may consist of titanium hydroxide or small quantities of sulphides of the copper and iron groups. Dilute the filtrate, and make it slightly acid with HCl. Shake to coagulate the precipitate, filter, and wash with hot water. Analyse the precipitate for the tin group by P. 42; reject the filtrate or test it for phosphate with molybdic acid.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 21st, 1907.

Prof. R. Meldola, F.R.S., President, in the Chair.

(Concluded from p. 117).

42. "*The Reduction Products of* o- *and* p-*Dimethoxybenzoin.*" By James Colquhoun Irvine and Agnes Marion Moodie.

o-Dimethoxybenzoin has been converted into the corresponding hydrobenzoin, and the latter compound, when reduced by Baeyer's process, gives *p*-dimethyltolane. This abnormal change has been shown to take place through the intermediate formation of *o*-dimethoxydiphenylethylene together with the corresponding ethane derivative.

As this result indicates that Baeyer's method of reduction may lead to erroneous conclusions in deducing the constitution of aromatic alkyloxy-compounds, a detailed study of the effect of the process on derivatives of anisoin has been made. It has been shown that both anisoin and its methyl ether are converted into deoxyanisoin when distilled with zinc-dust in a current of carbon dioxide, and that the reduction is only complete when carried out in an atmosphere of hydrogen. The hydrocarbon finally obtained was stilbene.

In the course of the work a number of new derivatives of anisoin were prepared and examined.

43. "*Constituents of Natural Indigo.*" (Part II.). By Arthur George Perkin.

Preliminary accounts of a portion of this work have previously appeared (*Proc.*, 1904, xx., 172; 1906, xxii., 199). The kaempferol glucoside, kaempferitrin, contained in the *Indigofera arrecta* is not hydrolysed by the insoluble indigo enzyme of Beyerinck (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 120), and its appearance in Java indigo is probably due to some extent to the employment of sulphuric acid at one stage of the manufacture. Numerous Java indigos have been examined, and all contained kaempferol, but in no case did this exceed 0·2 per cent. The leaves of the *Indigofera sumatrana* contain a trace of yellow colouring matter which probably consists of kaempferol.

44. "*The Velocity of Hydrolysis of Aliphatic Amides.*" By James Codrington Crocker.

The rates of reaction of formamide, acetamide, propionamide, butyramide, *iso*butyramide, valeramide, capronamide with hydrochloric acid have been determined at from 40° to 80°. The determinations were carried out by measurement of the specific conductivity of the reacting mixture. Owing to the effect of the dissolved amide on

the conductivity of the solution, the concentration could not be calculated directly from the specific conductivity. Synthetical mixtures were prepared representing definite stages of the reaction, and the variation of the specific conductivity of these with time was determined. By extrapolation to $t = 0$ the initial specific conductivity was determined in each case. A concentration-conductivity curve was plotted which served to standardise the original conductivity-time curve. The reactions are bimolecular, and follow the relation $K = \frac{1}{at}\left(\frac{1}{C} - \frac{1}{C^0}\right)$, where a is the degree of dissociation of the hydrochloric acid. The order of the relative reactivities is the same for each temperature; this order is formamide, propionamide, acetamide, *iso*butyramide, capronamide, butyramide, valeramide. The temperature coefficients of reactivity are very large, and the velocity constants closely follow the temperature law, $\log K = \log K_0 + B\left(\frac{1}{T} - \frac{1}{T}\right)$.

A relation between the reactivity of the amides at constant temperature and the strength of the corresponding organic acids was indicated. The relative reactivities of the amides were also evaluated at "corresponding" temperatures, and these values were shown to be nearly independent of temperature.

45. "*The Rusting of Iron.*" By Wyndham Rowland Dunstan.

As a result of a long series of experiments (Dunstan, Jowett, and Goulding, *Trans.*, 1905, lxxxvii., 1548), it was shown that the rusting of iron can take place in the absence of carbonic acid, and that only iron, oxygen and liquid water are necessary for rusting to occur. In order to elucidate the chemical change involved, and to explain the inhibiting effect on the rusting of iron produced by some substances and especially by alkalis and potassium dichromate, the working hypothesis was suggested that the formation of hydrogen peroxide is concerned in the change, rusting being prevented by those substances which are capable of decomposing the peroxide.

Recently, Dr. Gerald T. Moody (*Trans.*, 1906, lxxxix., 720) has published an account of experiments he has made which in his opinion prove that iron cannot rust in the absence of carbon dioxide. In the experiments recorded by the present author (*loc. cit.*) elaborate precautions were taken to ensure the absence of carbon dioxide, but it has been thought desirable to repeat the experiments made under somewhat different conditions by Dr. Moody. His conclusions have not, however, been confirmed; the results of experiments carried out in the manner described by him show that iron rusts freely in the absence of carbonic acid provided that iron, oxygen, and liquid water are brought together.

46. "*Contributions to the Chemistry of the Rare Earths.*" (Part II.) By Mario Esposito.

The methods of Muthmann and Böhm and Pattinson and Clarke for the preparation of ceria have been found to give a fairly pure product. Oxidation with potassium permanganate, according to Drossbach and Böhm's method, is probably the most rapid and satisfactory way of obtaining almost pure ceria.

Lanthana and old didymia can be separated by fractional crystallisation of the oxalates from strong nitric acid, but the process is not advantageous. Lanthana is best obtained by a modification of the method of Auer von Welsbach (fractional crystallisation of the double ammonium nitrates), which at the same time effects the separation of neodymia and praseodymia, the chief constituents of old didymia. After one hundred and ten fractionations, lanthana, praseodymia, and neodymia were obtained in a state of considerable purity.

47. "*Derivatives of Multivalent Iodine.* Part III. *Action of Heat on Iodobenzene Dichloride, and on the* m- *and* p-*Nitro- and* p-*Chloro-derivatives.*" By William Caldwell and Emil Alphonse Werner.

The authors have found that when iodobenzene dichloride is heated it undergoes sudden decomposition at 112—136° according to the rate of heating, the main change resulting in the formation of *p*-chloroiodobenzene. Only from 17 to 27 per cent of the theoretical amount of chlorine is evolved in the free state. Rapid heating favours the formation of the substitution derivative. Whilst *o*- and *p*-iodonitrobenzene dichloride, when heated, decompose quantitatively in accordance with the equation $C_6H_4(NO_2)\cdot ICl_2 = C_6H_4(NO_2)I + Cl_2$, the *m*-derivative loses from 72—73 per cent of its chlorine in the free state, a substitution derivative being produced in corresponding proportion.

p-Chloroiodobenzene forms a dichloride, $C_6H_4Cl\cdot ICl_2$, which decomposes at 112°, the proportion of chlorine evolved in the free state amounting to 72 per cent of the theoretical for the loss of two atoms. Thus the nitro-group in the ortho- and para-positions completely prevents the formation of substitution products, whilst chlorine in the para- has the same inhibiting effect as the nitro-group in the meta-position.

48. "*The Organic Phosphorus Compound formed by Yeast-juice from Soluble Phosphates.*" (Preliminary Notice). By William John Young.

It has been shown by Harden and Young (*Proc.*, 1905, xxi., 189; *Proc. Roy. Soc.*, 1906, B, lxxvii., 405) that when soluble phosphates are added to a fermenting mixture of yeast-juice and glucose a large increase in the rate of evolution of carbon dioxide is observed. This rate soon diminishes until a constant rate is attained, which is usually approximately equal to that of the original yeast-juice and glucose. It has been further shown that at the end of this period of increased fermentation, the phosphate has undergone some alteration, and is no longer present in the form precipitable by magnesium citrate mixture, and it was suggested that a combination with the glucose to form a phosphoric acid ester had taken place.

Experiments on the chemical nature of this compound have been carried out, and although not yet complete, it has been thought advisable to communicate a preliminary notice of the results so far obtained, in view of the publication of Iwanoff (*Zeit. Physiol. Chem.*, 1907, l., 281), who appears to have obtained the same substance independently.

A lead salt of the compound was prepared from the fermentation mixture by first removing any free phosphate by magnesium nitrate and then adding lead nitrate. Analyses of two preparations, in which the carbon, hydrogen, lead, and phosphorus were determined, gave the empirical formula $C_3H_5O_6PPb$.

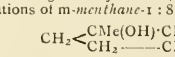
On suspending this salt in water and removing the lead with hydrogen sulphide, an acid solution is obtained which reduces Fehling's solution and gives Mohlisch's α-naphthol reaction. It is slightly dextrorotatory, and can be titrated with alkalis, using phenolphthalein as indicator, in a similar manner to phosphoric acid. On evaporating to dryness on the water-bath a charred mass is left, which contains free phosphoric acid, and has a strong odour of caramel, whilst on evaporation at the ordinary temperature in a vacuum over sulphuric acid a syrupy mass is left, which soon darkens in colour and decomposes.

When the solution is boiled for several hours the compound is slowly hydrolysed, phosphoric acid being set free, and a substance formed which reduces Fehling's solution more strongly than the acid itself, and rotates the plane of polarised light to the left. The nature of this reducing substance has not been exactly determined, and experiments with this object are in progress.

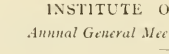
49. "*Experiments on the Synthesis of the Terpenes.* Part X. *Synthesis of Carvestrene and its Derivatives.*" By William Henry Perkin, jun., and George Tattersall.

Continuing their work on the synthesis of carvestrene

(*Proc.*, 1906, xxii., 268), the authors have prepared *m-cineol*,—



by the action of magnesium methyl iodide on ethyl *cyclo*hexanone-3-carboxylic acid, and the *cis*- and *trans*-modifications of *m-menthane*-1 : 8-*diol*,—



have also been obtained.

INSTITUTE OF CHEMISTRY.

Annual General Meeting, March 1st, 1907.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

THE financial statements for the year 1906 having been duly received, on the motion of Mr. A. GORDON SALAMON, Hon. Treasurer, seconded by Mr. THOMAS TYRER, Professor J. MILLAR THOMSON moved the adoption of the annual report of the Council, at the same time commenting on the recent work of the Institute. The Fellows now number 1016, and there are 177 Associates. The work of the Council and Committees during the year necessitated no less than 64 meetings, and the report contained several interesting items, such as the establishment of examinations in Chemical Technology, the further extension of the work of the Institute in the Colonies, the action taken by the Council in various matters affecting the interests of professional chemists, and the suggestion that the Intermediate and Final Examinations should be conducted by a board of Examiners, which appeared to him a step in the right direction.

Dr. W. A. TILDEN, in seconding the adoption of the report, cordially congratulated the Council on the progress made by the Institute in the past few years, but he remarked that the new developments, such as the Examinations in Chemical Technology and holding Examinations in the Colonies, were serious steps requiring very careful management.

The Report was then formally received and adopted.

The ballot for the election of Censors having been taken, the following were declared elected:—Professor Edward Divers, D.Sc., F.R.S.; Mr. David Howard; Sir William Ramsay, and Professor J. Millar Thomson, LL.D., F.R.S. The meeting proceeded to appoint the Honorary Auditors:—Messrs. W. T. Burgess and P. A. E. Richards being re-appointed, and Mr. Walter F. Reid being elected to the vacancy caused by the retirement of Mr. R. E. Alison.

The PRESIDENT then delivered his Address. After thanking the Fellows and Associates for electing him to the office of President, he said he valued the distinction not only for the confidence and good will of his colleagues which it implied, but also because it placed him in the Chair once occupied by his father, the late Sir Edward Frankland, K.C.B., F.R.S., the first President of the Institute. There was possibly an unconscious symbolism in his election, for it appeared to mark in the history of the Institute the passage from the first to the second generation; and while his predecessors in the Chair were all founders of the Institute, he had had to gain admission by examination. He remarked that the office of President had been no sinecure, but he had had the good fortune to succeed a President (Mr. David Howard) who justly enjoys a reputation as a man of affairs, and not only did he take over a carefully organised and going concern, but he had the benefit of his predecessor's valuable advice, for which he expressed his best thanks. He also acknowledged the services of the Chairmen of the various Committees. He then referred to the deaths of four distinguished Fellows:—Frederick Claudet, well known as an Assayer; Cornelius O'Sullivan, F.R.S., head of the brewing and scientific staff of Messrs. Bass and Co., of Burton-on-Trent; Charles Tookey, also an Assayer and Metallurgical Expert; and Dr. W. J. Sykes, the Editor of *The Analyst*. The most important feature of the year's work has been the inauguration of examinations in Chemical Technology. The first examination was held in October last, and was so successful that it dissipated any doubts which some may have entertained as to the value of these examinations. The Council believe that the institution of such examinations will materially help Fellows and Associates to obtain employment in chemical industries. Thanks were due to Dr. Ludwig Mond, F.R.S., the Chairman of the Chemical Technology Examinations Board, for valuable advice in connection with the scheme, and to Mr. Oscar Guttmann who had presented the Board with a collection of diagrams of plant and machinery which had been of great service in the oral examinations.

After referring to a number of changes made in the Regulations for admission to the Institute, particularly the deletion of Latin from the list of compulsory subjects in the Preliminary Examination, the President announced the appointment of a new Board of Examiners for the conduct of the Associateship examinations. The Board will be constituted as follows:—For the Intermediate Examination, Mr. Bertram Blount and Dr. G. G. Henderson; for the Final Examinations, Mineral Chemistry, Mr. Bertram Blount; Metallurgical Chemistry, Mr. F. W. Harbord; Physical Chemistry, Dr. T. Slater Price; Organic Chemistry, Dr. G. G. Henderson; the Analysis of Food and Drugs and of Water, Mr. Cecil Cribb; Biological Chemistry, Dr. A. Harden; Therapeutics, Pharmacology, and Microscopy, Dr. F. Gowland Hopkins, F.R.S. The President was sure that the Board thus constituted would make for efficiency, and that it would be difficult to find anywhere more powerful machinery for conducting chemical examinations.

He then referred to the growth of the Library of the Institute, which is mainly supported by the contributions of the Fellows. The Library is essentially a working library, as distinguished from the exhaustive libraries, such as that of the Chemical Society, which the Institute did not wish to attempt to duplicate. Yet another piece of work accomplished was the publication of a List of Official Chemical Appointments, which the President considered one of the most useful publications that had ever emanated from the office of the Institute.

An important function of the Institute is to safeguard the interests of professional chemists. During the past year, the Council had devoted much time to work of this kind, particularly in connection with the appointments of analysts under the Fertilisers and Feeding Stuffs Acts, and the Sale of Food and Drugs Acts. Special thanks are due to Sir William Ramsay, K.C.B., the Chairman of the Public Appointments Committee, which had charge of these matters. If all young chemists were aware of the amount of time and trouble spent by the Council in endeavouring to secure better conditions for professional chemists of every kind, many more would take the examinations and support the Institute in its work.

The President concluded his Address by commenting on the special value of the qualifications of the Associateship and Fellowship of the Institute, and he showed how the examinations of the Institute differed from those of the universities. The latter are contrived to test the amount of knowledge which a candidate has succeeded in bringing to a focus at a particular moment of time, whilst the main object of the examinations of the Institute is to test what the candidate can actually perform when he is placed as nearly as possible under the same conditions as he would be if working in his own laboratory and within reach of a good chemical library. The candidate who shines in the one will not necessarily shine in the other. It is a common

experience for teachers to meet with students of excellent mental ability who readily acquire knowledge of theoretical chemistry even in its more advanced and modern branches, and who talk glibly about the phase rule, the ionic theory, and even the electronic theory of matter, and perhaps can cite correctly author and year for the disovery of reactions in obscure chapters of organic chemistry; yet when it comes to the production of experimental results with their own hands, are hopelessly outclassed by students of more modest theoretical attainments; and whilst the latter meet with remarkable success in their practical work, everything fails in the hands of those who move with such facility in the theoretical part of the subject. The paper man takes, in all probability, an Honours Degree, but should he present himself at the Institute he may ignominiously come to grief because he does not possess even the rudiments of that instinct which is still necessary to the performance of practical chemical work, in spite of the application of higher mathematics to the interpretation of chemical phenomena. Before all things, the Institute's qualification is of a practical nature. The University graduate is more qualified to talk and to teach, but the overcrowding of his curriculum leaves him little time in which to practise and acquire technical skill, without which the Institute's qualification cannot be attained at all. It is this practical character which must be preserved in the Institute's examinations, so that the Fellows and Associates may be known for the soundness of their judgment and for their capacity to perform chemical work upon which the public can place implicit reliance. The Institute must be ever ready to extend the scope of its examinations as new branches of chemistry arise, and in each branch must secure the highest standard of excellence.

On the motion of Mr. R. J. Friswell, seconded by Dr. Edward Divers, F.R.S., a hearty vote of thanks was accorded to the President for his Address.

The Officers and Members of Council for the ensuing year were duly elected as follows:—

President—Percy Faraday Frankland, LL.D., Ph.D., F.R.S.

Vice-Presidents—Edward John Bevan; Edward Divers, M.D., D.Sc., F.R.S.; Oscar Guttmann, M.Inst.C.E.; David Howard; Herbert Jackson; Sir William Ramsay, K.C.B., LL.D., F.R.S.

Hon. Treasurer—Alfred Gordon Salamon, A.R.S.M.

Members of Council—Adrian John Brown, M.Sc.; Russell Forbes Carpenter; Charles Edward Cassal, Col.; John Clark, Ph.D.; Arthur Crozier Claudet, A.R.S.M.; John Norman Collie, Ph.D., F.R.S.; Cecil Howard Cribb, B.Sc.; Bernard Dyer, D.Sc.; Henry John Horstman Fenton, M.A., Sc.D., F.R.S.; Walter William Fisher, M.A.; Martin Onslow Forster, D.Sc., Ph.D., F.R.S.; William Gowland, A.R.S.M.; Henry George Greenish; Egbert Grant Hooper; Arthur Robert Ling; William Macnab; Gerald Tattersall Moody, D.Sc.; Henry de Mosenthal; Henry Droop Richmond; Alfred Smetham; Arthur Smithells, B.Sc., F.R.S.; John Edward Stead, F.R.S.; Francis Napier Sutton; Oliver Trigger; John Augustus Voelcker, M.A., Ph.D., B.Sc.; Alexander Forbes Watson, B.Sc.; William Palmer Wynne, D.Sc.; F.R.S.

With a cordial vote of thanks to the retiring Officers and Members of Council for their services, moved by Mr. Walter Reid and seconded by Mr. R. Forbes Carpenter, to which Mr. Friswell responded, the meeting terminated.

Appointments.—The vacant posts in the Metallurgical Department of the National Physical Laboratory have been filled by the appointment of Mr. J. Murdoch as Senior Assistant, and Mr. S. L. Archbutt as Junior Assistant.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 8, February 25, 1907.

The Lactyllactate of Ethyl.—M. Godchot and E. Jungfleisch.—In their researches upon the lactic acids, the authors found that the facts observed could not be accounted for by any usually defined reactions in connection with complex ethers; but it was found further that they admitted of interpretation upon considerations of a general order. The case here described, a relatively simple one, is that of the products furnished by the action of heat upon ethyl (*d* + *l*) lactate. The heating is carried out in sealed tubes at 250° for seven or eight hours, followed by distillation *in vacuo*. The products obtained are as follows:—(1) Ethyl alcohol; (2) towards 65—70°, ethyl lactate; (3) between 110—120°, a colourless syrupy liquid, being the bulk of the remainder; (4) towards 140—150°, a faintly yellow liquid. The third product boils at 215—220° at normal pressure; it has an ethereal odour, and is a colourless liquid of density 1·096 at 0°. It shows the composition of ethyl lactyllactate:— $CH_3—CH(OH)—CO_2—CH(CH_3)—CO_2—C_2H_5$. It has a molecular weight of 199 by the cryoscopic method, the theoretical figure being 192. In its properties the body resembles the monoethyl dilactate described by Wurtz and Friedl in 1861, and obtained by the action of potassium lactate on chloropropionic ether; but the ethyl lactate mixes rapidly with cold water and is saponified by it, while ethyl lactyllactate remains in contact with cold water without being sensibly dissolved by it, and in warm water it disappears slowly with formation of lactic acid. The production of ethyl alcohol with the lactyl-lactate by the action of heat upon ethyl lactate gives the key to the solution of the reaction, the ethyl alcohol of one molecule of ethyl lactate being displaced by the lactic alcohol of another molecule:— $CH_3—CH(OH)—CO_2—C_2H_5 + OH—CH(CH_3)—CO_2—C_2H_5 = CH_3—CH(OH)—CO_2—CH(CH_3)—CO_2—C_2H_5 + C_2H_5—OH$. It is worthy of notice that ethyl lactyllactate is relatively more stable than lactyllactic acid. The fourth product of distillation, obtained between 140° and 150°, boils at 250—260° at normal pressure; it is a syrupy liquid, furnishing crystals when cooled, and these have the same melting-point and properties as the (*d* + *l*)-dilactide. Its formation may be represented thus:—

$$CH_3—CH(OH)—CO_2 \quad = \quad C_2H_5—CO_2—CH(CH_3)—CO_2—CH(CH_3)—CO_2—CH(CH_3)—CO_2—C_2H_5 + OH—C_2H_5.$$

Hence, the products of this reaction with ethyl lactate are found to be analogous to those obtained by heating lactic acid, but the mechanism of the transformations is different. These facts are of a general nature, and apply to similar reactions with ethers of other complex acids.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture arrangements at the Royal Institution after Easter:—Professor G. H. Bryan, two lectures on "Wings and Aeroplanes"; Professor W. Stirling, three lectures on "Stimulation, Luminous and Chemical"; D. S. MacColl, Esq., two lectures on "Alfred Stevens (the English Sculptor and Painter)"; Professor G. H. F. Nuttall, two lectures on "Malaria, Sleeping Sickness, Tick Fever, and Allied Diseases"; Professor H. A. Miers, two lectures on "The Birth and Affinities of Crystals"; Dr. A. W. Werrell, two lectures on (1) "Euripides and his Age, (2) The Bacchants of Euripides"; H. F. Newall, Esq., two lectures on "Spectroscopic

Phenomena in Stars, (1) Chemistry, (2) Motion"; Professor Sir James Dewar, three lectures on "Chemical Progress—Work of Mendeleeff and Moissan"; Professor S. P. Thompson, three lectures on "Studies in Magnetism (the Tyndall Lectures)"; Professor W. C. McIntosh, two lectures on "Scientific Work in the Sea Fisheries"; Arthur Bourchier, Esq., two lectures on "The Limits of the Dramatic Art"; and Sir William H. White, two lectures on "The Contest between Guns and Armour." The Friday Evening Meetings will be resumed on April 12th, when a Discourse will be given by Professor A. H. Church on "Conservation of Historic Buildings and Frescoes (with Experimental Illustrations)"; succeeding Discourses will probably be given by Professor C. S. Sherrington, James Swinburne, Esq., Sir James Crichton-Browne, Signor Comè Giacomo Boni, Professor G. Chrystal (assisted by E. M. Wedderburn, Esq.), Professor J. A. Fleming, A. H. Savage Landor, Esq., Professor Sir James Dewar, and other gentlemen.

MEETINGS FOR THE WEEK.

TUESDAY, 19th.—Royal Institution, 3. "The Visual Apparatus of Man and Animals," by Prof. William Stirling.
— Society of Arts, 8. "Oils, Varnishes, and Mediums Used in the Painting of Pictures," by A. P. Laurie.
— Faraday Society, 8. "Potential of Hydrogen liberated from Metallic Surfaces," by H. Nutton and H. D. Law. "Electrode Potentials in Liquid Ammonia," by F. M. G. Johnson and N. T. M. Wilsmore. "The Impedence of Solutes in Solvents as manifested by Osmotic Pressure," by J. G. A. Rhodin. "Electrolytic Deposition of Zinc, using Rotating Electrodes," by T. S. Price.

WEDNESDAY, 20th.—Society of Arts, 8. "Smoke Prevention in Factories and Electric Supply Stations," by J. B. C. Kershaw, F.I.C.
— — Microscopical, 8. "Some South African Tardigrada," by James Murray. Exhibition of Specimens of British Mycetozoa, by Alfred E. Hilton.

THURSDAY, 21st.—Royal Institution, 3. "Biology and Progress," by Dr. C. W. Saleeby, F.R.S.E.
— Chemical, 8.30. "Synthesis of Polypeptides," by E. Fischer. "Organic Derivatives of Silicon—Part III., *dl*-Benzylmethylethylpropylsilicane and Experiments on the Resolution of its Sulphoxic Derivative," by F. S. Kipping. "Reduction of Carbon Dioxide to form Aldehyde in Aqueous Solutions," by H. J. H. Fenton. "Mechanism of the Rusting of Iron," by G. T. Moody. "Some Compounds of Guanidine with Sugars," by S. S. Morrell and A. E. Bellars.

FRIDAY, 22nd.—Royal Institution, 9. "Rays of Positive Electricity," by Prof. J. J. Thomson, F.R.S., &c.
— Physical, 5. "Experimental Mathematics," by Mr. Pochin. "Logarithmic Lazytongs and Lattice Works," by Mr. Blakesley. "A Micromanometer," by Mr. Roberts. "Electrical Conduction produced by Heating Salts," by Mr. Garrett.

SATURDAY, 23rd.—Royal Institution, 3. "Röntgen, Cathode, and Positive Rays," by Prof. J. J. Thomson.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2469.

EXISTENCE OF AMMONIUM HYDRATE.

By PHILIP BLACKMAN.

It was shown by the author ("Quantitative Relation between Molecular Conductivities," *Phil. Mag.*, 1906, xi., 116; Chemical News, 1906, xciv., 164) that, at constant temperature,—

$$\begin{aligned}\mu_{v M_1OH} - \mu_{v M_2OH} &= \mu_{v M_1X} - \mu_{v M_2X} \\ &= \mu_{v M_1X_1} - \mu_{v M_2X_1} \\ &= \mu_{v M_1X_2} - \mu_{v M_2X_2} \\ &= \ldots\ldots\ldots\ldots \\ &= \text{constant}\end{aligned}$$

(in which μ_v represents the molecular conductivity at concentration v of the bases M_1OH and M_2OH, and of the salts M_1X, M_2X, &c.).

In the case of ammonium hydrate, NH_4OH, and of ammonium salts, NH_4X, NH_4X_1, &c., the above expression is true for the salts only, the quantity $\mu_{v NH_4OH} - \mu_{v M_2OH}$ not being equal to this constant, as is illustrated in Table I. (constructed from the data in Landolt-Bornstein's "Physikalisch-Chemische Tabellen," 1905 edition).

The molecular conductivities of the potassium salts are almost the same as those of the corresponding ammonium salts, and the expression $\mu_{v KX_n} - \mu_{v NH_4X_n}$ is consequently near zero in value. It would be very reasonable to expect that the molecular conductivities of potassium and ammonium hydrates would also have been almost identical in value (when measured under the same conditions of temperature and concentration).

By means of the equation—

$$\mu_{v NH_4OH} = \mu_{v M_2OH} + \mu_{v NH_4X_n} - \mu_{v M_2X_n}$$

it is possible to calculate the "theoretical" molecular conductivities of ammonium hydrate (Table II.).

From an examination of the above facts the following is a most reasonable conclusion:—

If the ammonia in aqueous solution were entirely converted into ammonium hydrate, then the experimental values for the molecular conductivities would be near the calculated theoretical values. But as the experimental values are far below the theoretical ones, we must conclude that the ammonia in aqueous solution exists only partially as ammonium hydrate. Accordingly, the percentage of ammonia existing as ammonium hydrate in aqueous solution is given by the formula—

$$100\ \frac{\text{Experimental } \mu_{v NH_4OH}}{\text{Theoretical } \mu_{v NH_4OH}}.$$

By the aid of this formula Table III. has been compiled.

Table IV. is an additional illustration of the foregoing argument and conclusion.

Table IV.

	v (at 25°) =	512	256	128
$\mu_v NH_4Cl - \mu_v TlCl$		0·9	1·3	2·5
But $\mu_v TlOH - \mu_v NH_4OH$		220·5	229·0	230·6
$\mu_v TlOH + \mu_v NH_4Cl - \mu_v TlCl$		248·9	249·3	246·5
Experimental $\mu_v NH_4OH$		27·5	19·0	13·4
Cf. $\mu_v NH_4 + \mu_v OH$ (Chem. News, 1906, xciv., 176)		248·0	245·0	244·0
Percentage of NH_4OH		11·0	7·62	5·4

The accompanying tables would seem to indicate that the percentage of ammonia in aqueous solution existing as ammonium hydrate increases with increased dilution. With the present limited data at one's disposal, it is impossible to determine definitely by the preceding method whether rise in temperature causes an increase or diminution in the percentage amount of ammonium hydroxide.

Thus, though ammonium hydrate is theoretically as strong a base (on the electrical conductivity theory) as potassium hydroxide, yet, because of the small quantity of ammonia existing as the hydrate in aqueous solution, it is in practice one of the weakest bases. But this view renders it difficult to explain the great solubility of ammonia in water.

The author is indebted to Prof. Dr. R. Luther, of Leipzig, for the following (from "If one . . . " to " . . . = $K_{Blackman}$"):—

If one grm.-molecule of ammonia be dissolved in water to give v litres of the solution, and the proportion of it converted into ammonium hydrate be denoted by q, the concentrations of the combined ammonia, uncombined ammonia, combined water, and uncombined water are respectively—

$$\frac{q}{v},\quad \frac{1-q}{v},\quad \frac{q}{v},\quad \text{and}\quad 1-\frac{q}{v}.$$

(The letter c denotes "concentration" and K a "constant"). According to the "electrolytic dissociation" theory, $K c_{NH_4OH} = c_{NH_4} \times c_{OH}$ (K$_e$ = "electrolytic" constant). 2.

$$K_h c_{NH_4OH} = c_{NH_3} \text{ (K}_h\text{ = "hydrolytic" constant)}. \quad . \quad . \quad 1,$$

$$c_{NH_4} = c_{OH} = \frac{\mu_v}{v\mu_\infty} = \frac{a}{v_{Ostwald}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 3,$$

$$= \text{approximately } \frac{\text{Experimental } \mu_v}{v.\ \text{Theoretical } \mu_v} = \frac{q}{v_{Blackman}} \quad . \quad 3a.$$

$$c_{NH_4OH} + c_{NH_3} = c_{\text{non conducting ammoia}} = \frac{1-a}{v_{Ostwald}} = \text{nearly} \frac{1-q}{v_{Blackman}}$$

$$c_{NH_4OH} + c_{NH_3} = c_{\text{non-conducting ammonia}} = (1+K_h) c_{NH_4OH} \text{ (from Equation 1)}$$

$$= \frac{1-a}{v_{Ostwald}} = \text{approximately } \frac{1-q}{v_{Blackman}}.$$

$$c_{NH_4OH} = \frac{1-a}{v} \cdot \frac{1}{1+K_h\ Ostwald}.$$

From Equations 2, 3, and 3*a* we obtain—

$$\frac{K_e}{1+K_h} = \frac{a^2}{(1-a)v_{Ostwald}} = K_{Ostwald}$$

$$= \frac{q^2}{(1-q)v_{Blackman}} = K_{Blackman}.$$

(Prof. Dr. R. Luther has subsequently pointed out to me the analogous work of Prof. Dr. F. Walker, *Journ. Chem. Soc.*, 1903; *Trans.*, lxxxiii., 182. His work above is independent of Dr. Walker's research.—P. B.).

Tables V. and VI. illustrate the similarity between these two constants.

Table V.

v (at 18°).	K (Blackman) × 10⁵.	K (Ostwald) × 10⁵.
1000	1·69	1·60
500	1·79	1·86
200	1·79	1·66
100	1·93	1·75
50	2·11	2·34
20	2·25	2·08
10	2·23	1·99
2	2·47	1·69
1	2·51	1·61
Mean	2·09	1·84

TABLE I.

v (at 18°) =	1000	500	200	100	50	20	10	2	1
$\mu_v KCl - \mu_v NH_4Cl$	0·0	0·1	0·2	0·3	0·3	0·5	1·3	1·0	1·3
$\mu_v KNO_3 - \mu_v NH_4NO_3$	0·9	0·4	0·9	0·2	2·2	0·2	1·4	5·1	8·4
$\mu_v \frac{1}{2}K_2SO_4 - \mu_v \frac{1}{2}(NH_4)_2SO_4$								2·9	3·4
$\mu_v KI - \mu_v NH_4I$								0·1	0·5
But $\mu_v KOH - \mu_v NH_4OH$	206	203·4	216·8	219·4	217·9	214·4	209·7	195·7	183·1
$\mu_v NH_4Cl - \mu_v NaCl$	20·8	20·7	20·4	20·2	20·0	19·5	18·7	19·1	21·2
$\mu_v NH_4NO_3 - \mu_v NaNO_3$	21·7	21·1	19·5	19·8	17·5	18·6	19·4	19·0	21·4
$\mu_v \frac{1}{2}(NH_4)_2SO_4 - \mu_v \frac{1}{2}Na_2SO_4$ ..								19·7	19·8
$\mu_v NH_4I - \mu_v NaI$								22·2	24·4
But $\mu_v NaOH - \mu_v NH_4OH$	177	182·9	191	193·6	194·1	194·4	192·1	172·7	156·1
$\mu_v NH_4I - \mu_v LiI$								29·8	32·5
$\mu_v \frac{1}{2}(NH_4)_2SO_4 - \mu_v \frac{1}{2}Li_2SO_4$ ..								22·8	25·7
$\mu_v NH_4Cl - \mu_v LiCl$								30·7	33·6
But $\mu_v LiOH - \mu_v NH_4OH$								136·6	124·5

TABLE II.

				v (at 18°) =	1000	500	200	100	50	20	10	2	1
$\mu_v KOH$	+ $\mu_v NH_4Cl$	− $\mu_v KCl$	..		234·0	232·9	229·8	227·7	224·7	218·5	211·7	196·0	183·7
KOH	+ NH_4NO_3	− KNO_3	..		234·9	234·8	229·1	227·8	222·8	219·2	214·8	202·1	192·4
NaOH	+ NH_4Cl	− NaCl	..		225·8	225·2	224·2	223·6	221·1	219·5	214·1	179·8	162·0
NaOH	+ NH_4NO_3	− $NaNO_3$	..		226·7	225·6	223·7	223·2	218·5	217·6	214·8	194·5	179·9
NaOH	+ NH_4I	− NaI	..									196·3	181·4
KOH	+ NH_4I	− KI	..									193·2	175·3
KOH	+ $\frac{1}{2}(NH_4)_2SO_4$	− $\frac{1}{2}K_2SO_4$	..									187·7	187·0
NaOH	+ $\frac{1}{2}(NH_4)_2SO_4$	− $\frac{1}{2}Na_2SO_4$	..									188·4	173·8
Average theoretical $\mu_v NH_4OH$			.. .. ..		230·1	229·3	226·7	225·6	221·8	218·7	213·8	192·2	179·3
Experimental			,, ...		28·0	20·6	13·2	9·6	7·1	4·6	3·3	1·35	0·9
Cf. $\mu_v NH_4 + \mu_v OH$ (*Phil. Mag.*, 1906, xii., 150—152)					228	224	222	219	216	210	199	186	172

TABLE III.

v (at 18°) =	1000	500	200	100	50	20	10	2	1
Percentage of NH_4OH ..	12·2	9·0	5·8	4·3	3·2	2·1	1·5	0·7	0·5

TABLE VI.

v (at 25°).	K (Blackman) × 10³.	K (Ostwald) × 10³.
512	2·66	2·65
256	2·46	2·44
128	2·41	2·37
Mean	2·51	2·49

According to the "law of mass action," we have—

$c$uncombined ammonia × $c$uncombined water = $k \times c$ombined NH_3,

or—

$$\frac{1}{k} = K = \text{constant} = \frac{q}{v}\left(\frac{v}{1-q}\right)\left(\frac{v}{v-q}\right) = \frac{vq}{(1-q)(v-q)}.$$

On performing the calculations, the values for K thus obtained are not the same for different concentrations:—

v (at 18°) =	1000	500	200	100	50	20	10	2	1
$K \times 10^2$ =	13·89	9·89	6·15	4·49	2·39	2·14	1·49	0·7	0·5

v (at 25°) =	512	256	128
$K \times 10^2$ =	12·35	8·25	5·72

East London College, London, E.

THE OCCLUSION OF THE RESIDUAL GAS BY THE GLASS WALLS OF VACUUM TUBES.*

By A. A. CAMPBELL SWINTON.

USERS of Crookes's tubes for Röntgen ray purposes have for long been aware that, apparently owing to a change in vacuum, the tubes become "harder" with use, and that it becomes necessary in the case of old tubes to heat the glass in order to get the discharge to pass.

In a paper read before the Royal Society in April, 1899 ("On the Luminosity of the Rare Earths when Heated *in vacuo* by means of Cathode Rays," *Proc. Roy. Soc.*, vol. lxv.), the present writer pointed out that the vacuum actually increases in cathode ray tubes with use, even if repeated small doses of additional air be let in from time to time.

Villard has also shown that the residual gas in a vacuum tube is driven into the glass, and that portions of the glass of a tube that has been used show bubbles if heated strongly. Again, in a paper on the absorption of gas in a Crookes's tube by Dr. R. S. Willows (*Phil. Mag.*, April, 1901), a number of experiments relating to this subject are

* A Paper read before the Royal Society, February 28, 1907.

recorded, including one by Professor J. J. Thomson, in which, after admitting small quantities of air and absorbing the same repeatedly, it was found that the weight of the tube had increased by the weight of the air that had been admitted, although after admission the discharge caused the pressure to fall so much that Röntgen rays were given off by the tube.

The present paper describes certain further investigations on this subject.

The tubes first experimented upon were some of those originally employed by the writer in 1898, and referred to in his above-mentioned paper. Since that date they have been lying undisturbed and open to atmospheric pressure, so that the gas now found to be imprisoned in the glass must have been there for some nine years. No note was taken in 1898 as to the amount of time that the tubes were used, but each was in operation for many hours and under extremely severe conditions, the alternating current employed having a volume of some 20 milli-ampères at about 8000 volts pressure.

The condition of the glass walls of these tubes is now found to be as follows:—When cleaned by rubbing they are quite transparent to casual inspection, though careful examination with the microscope shows that the inner surface of those portions that had been subjected to cathode ray bombardment are materially roughened. When these portions of the glass are strongly heated in a blowpipe flame, they immediately become clouded, the effect being due to quantities of minute spherical bubbles in the glass, which may clearly be seen with a microscope. The bubbles vary to some extent in size, but on the average are about 0·01 mm. in diameter. They are usually packed closely together in a single layer, and are always very near the side of the glass that formed the inner surface of the tube. On measuring the thickness of the glass with a micrometer gauge, dissolving the inner surface with hydrofluoric acid until the bubbles had just disappeared, and then again measuring the thickness, it was found that, after making allowance for the size of the bubbles, the centres of these bubbles were about 0·122 mm. from the inner surface of the glass. A similar estimate was obtained by grinding the inner surface of the glass until the bubbles just disappeared, and making micrometer measurements as before. It would therefore appear that the particles of gas must have been shot into the glass to about the depth stated.

In a typical piece of glass the number of bubbles per square centimetre of glass was found to be about 625,000, so that, allowing for the expansion of the gas on heating the glass up to redness, there was occluded about 0·000113 cc. of gas at atmospheric pressure per square centimetre of glass, and as the amount of glass surface that was bombarded in each tube was about 400 sq. cm., the total amount of gas at atmospheric pressure occluded in each tube is nearly 0·05 cc., apart from any further amount that may have escaped from the glass in the heating of the latter.

An interesting question arises as to whether the gas is merely mechanically mixed with the glass or whether there has been any chemical combination between the two. In the latter case, it seemed unlikely that mere powdering of the glass would cause the gas to come out, while in the former case it seemed probable that powdering the glass would have this effect.

In order to test this, a number of pieces of the glass were placed in a chamber consisting of two slightly dished tinned plates some 15 cm. in diameter, which was soldered together all round the edges, with a metal tube inserted, so as to be air-tight. The chamber was connected with a mercury pump and a spectrum tube, and was then pumped until no electric discharge could be got to pass through the spectrum tube. An anvil was then placed under the chamber, and the latter was struck several blows with a hammer so as to powder the glass, when there was an immediate fall of vacuum, and on examination with a spectroscope the gas that had been evolved was found to be mainly hydrogen. The chamber was then pumped out again, and on further blows being struck so as to powder more glass, similar results were obtained; in fact, the process was repeated many times, the result being in each case to bring out more hydrogen.

It would appear therefore that the gas occluded in soda glass vacuum tubes exhausted in the ordinary manner from air is almost entirely hydrogen, no doubt due to electrolysis of water vapour condensed on the walls of the tube prior to exhaustion, the oxygen of which is absorbed by oxidation of the aluminium electrodes.

In order, further, to determine whether the occlusion of gas in a vacuum tube is in any way due to chemical combination of the gas with the glass, or whether it is purely a case of the gas being driven into the glass and mechanically held there, a suggestion made to the writer by the Hon. R. J. Strutt was followed, and experiments were tried with helium.

A spherical tube of soda-glass about 7 cm. in diameter, with two electrodes consisting of aluminium plates, was employed. The tube was first exhausted in the ordinary way from air until the vacuum was so high that the discharge would not pass, and then, by an arrangement of stop-cocks, a small quantity of helium was admitted. The tube was then sparked, and the vacuum was found to increase, showing that the helium was being absorbed. Further small quantities of helium were admitted at intervals, the process being continued intermittently for twenty days, the total number of hours of sparking being about ninety, or four and a-half hours per day, and the number of admissions of helium about 700, until about 1 cc. of helium at atmospheric pressure had been absorbed.

During the process of sparking the tube gradually blackened, the deposit being afterwards ascertained to be aluminium from the electrodes. There thus seemed some doubt as to whether the helium was being absorbed entirely by the glass or perhaps partly by the very thin coating of aluminium, which, by the time the cc. of helium had been absorbed, had become a perceptible mirror.

On breaking up the tube, however, it was found that whether the glass was heated without further treatment, or whether the mirror of aluminium was first dissolved off its surface with dilute nitric acid, a plentiful supply of bubbles was produced in the glass, showing that at any rate some portion of the helium had found its way into the latter. In appearance the bubbles were very similar to those that had been found in the tubes that had occluded hydrogen, only, as a rule, the bubbles were more numerous and considerably smaller in diameter. Furthermore, as a rule, they tended to be gathered together in groups, and were not evenly distributed over the glass as in the case of hydrogen. Under these circumstances, it was very difficult to estimate the quantity of gas occluded in the glass. It was certainly much less than in the case of hydrogen, and only a fraction of the 1 cc. occluded altogether. The remainder would seem not to have been driven far enough into the glass to form bubbles, but to have escaped from the surface on the glass being heated.

Similar experiments were made with the glass containing helium to those tried with the glass containing hydrogen, in the way of extracting the gas by powdering the glass in a vacuum chamber. It was found impossible to get rid altogether of the hydrogen spectrum and other faint lines, due, no doubt, to impurities, but, on the glass being powdered, the helium spectrum was found to be clearly superposed. This was equally the case when glass that was still coated with the aluminium deposit was used as with glass from which this deposit had been dissolved off. Consequently, the occlusion appears to take place entirely in the glass.

Seeing that helium does not combine with anything at ordinary temperatures, and seeing further that it could be extracted from the glass by the mere mechanical powdering of the latter, it would appear that the occlusion is due to the mechanical driving of the gas into the glass and not to any chemical combination.

The writer is indebted to Mr. J. C. M. Stanton and Mr. R. C. Pierce for their assistance in carrying out the investigations.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 128).

Procedures and Notes (continued).

Procedure 5. (For an alternative procedure, see N. 7 below and P. 8).—Transfer to a platinum crucible the residue after treatment with acids (P. 2 or P. 4), add 2 cc. H_2SO_4 (1·84) from a graduate, heat with a moving flame until white fumes are given off, and cool completely. To test for silica, add carefully (see N. 1) from the loop of a platinum wire pure 40 per cent HF drop by drop until 5 to 6 drops have been added, and warm the mixture over a steam-bath. (Formation of gas bubbles, presence of *silica*).

Then add about 5 cc. more pure 40 per cent HF, cover the crucible with a platinum cover, digest on a steam-bath for about fifteen minutes unless the residue dissolves more quickly; remove the cover and evaporate carefully until white fumes of H_2SO_4 are given off, heating the sides of the crucible with a moving flame—or, better, with a ring-burner to avoid spattering. (Unless it is known from the presence of solid substance at this point or from previous observations that the residue treated with H_2SO_4 and HF contained other constituents than silica, determine this by evaporating off the H_2SO_4 under a hood, taking care not to ignite the residue. If a significant residue remains, add from a graduate 1·5 cc. H_2SO_4 (1·84), and heat until the residue is re-dissolved, not allowing the acid to evaporate). Cool, pour the contents of the crucible into 10 cc. water, and rinse out the contents with a little water. Boil to dissolve slowly-dissolving sulphates; cool, shake, filter, and wash the residue, first with H_2SO_4 (1·20) and then with a little water, rejecting the washings. (Residue, P. 6). To the filtrate add HCl drop by drop only as long as a precipitate forms; filter, wash the precipitate, and test it for silver by P. 15. Dilute the filtrate to a volume of 40 cc., treat it with H_2S by P. 21, subsequently testing for all the metallic elements except lead, barium, and strontium.

Notes.

1. Great care must be taken not to breathe the fumes of HF nor to get it on the hands; for it is very irritating and produces dangerous burns.

2. The test for silica or silicate depends on the formation of SiF_4 gas, which is insoluble in strong H_2SO_4, but dissolves in water in the presence of HF with formation of fluosilicic acid, H_2SiF_6. With free silica the evolution of gas takes place in the cold; but with slowly decomposing silicates, such as felspar, the test is obtained only upon warming. A few silicates are not acted upon by HF and H_2SO_4, and of course do not show the test for silica at this point. The test is delicate enough to enable 1 mgrm. of silica, whether free or in a decomposable silicate, to be detected. Moreover, after the substance has been treated with acids as in P. 4 and warmed with H_2SO_4, an evolution of gas with HF is not produced with the compounds of any element other than silicon (not even with those of titanium, niobium, and tantalum, which form somewhat volatile fluorides). It should be borne in mind that a small quantity of silica will be introduced if ordinary filters (which have not been washed with HF) have been employed and have been destroyed by acids or by ignition, or if a strongly alkaline solution has been boiled in glass vessels, or if a substance has been fused with sodium carbonate in a porcelain crucible.

3. Since glass and porcelain consist of silicates which are readily attacked by HF, this acid must not be allowed to come into contact with these materials. In handling cold HF solutions, vessels and funnels of celluloid or paraffin or of glass coated with paraffin may be used; but platinum vessels must be employed when the solutions are to be heated. Care must be taken not to introduce into a platinum vessel any solution containing chlorine or bromine or any acid mixture containing nitrates and chlorides by which chlorine would be evolved. Platinum is so slowly attacked by hot concentrated H_2SO_4 that even when 2 to 3 cc. of the acid are rapidly evaporated in a crucible less than half a milligrm. passes into solution; but, if the acid is boiled for ten to fifteen minutes in a covered vessel, 2 or 3 m.grms. may be dissolved, and would be precipitated subsequently by H_2S.

4. The digestion with HF decomposes most silicates and dissolves silica (and much titanium oxide). The subsequent evaporation with H_2SO_4 expels the excess of HF and decomposes the fluorides produced, as well as some other substances that may have been left undissolved by the HNO_3 and HCl. The H_2SO_4 solution is diluted with a small quantity of water, so as to cause the complete precipitation of $BaSO_4$, $SrSO_4$, and $PbSO_4$. These sulphates are moderately soluble in strong H_2SO_4 and may not appear till after dilution. The addition of much water is avoided, since $SrSO_4$ and $PbSO_4$ are somewhat soluble in water; and the residue is washed with dilute H_2SO_4 for the same reason. The solution is boiled so as to dissolve anhydrous sulphates, such as those of aluminium and iron.

5. The residue insoluble in dilute H_2SO_4 contains as sulphates all the barium, strontium, and lead, and all of the calcium in excess of 5 to 10 mgrms. left undissolved by HNO_3 and HCl; more or less of the chromium (according as the H_2SO_4 has been more or less strongly heated) as a pink anhydrous sulphate; and part of the bismuth as basic sulphate and antimony as antimonic hydroxide, when much of these elements were left undissolved by the previous treatments with acids. The residue may also contain still undecomposed substances, especially the following:—Silver chloride; corundum, Al_2O_3; chromite, $FeCr_2O_4$; cassiterite, SnO_2; rutile, TiO_2; tungstic oxide, WO_3; molybdenum sulphide, MoS_2; some anhydrous silicates and fluosilicates, such as cyanite or andalusite (Al_2SiO_5) and tourmaline; graphite and carbides.

6. If the presence of silver is shown by the addition of HCl, the residue insoluble in dilute H_2SO_4 is likely to still contain AgCl, which is only slowly decomposed by hot concentrated H_2SO_4. In order to dissolve this, add to the residue in a small casserole 3 to 5 cc. concentrated H_2SO_4, heat until white fumes are given off, cover the dish with a large watch-glass, and boil gently for five to ten minutes. Cool, and treat as described in the last paragraph of the above procedure. If AgCl is not completely removed in this way, its presence will be shown by a blackening of the residue upon boiling with Na_2CO_3 solution in P. 6; in such a case it must be removed by further treatment with H_2SO_4 before a fusion with Na_2CO_3 is made in a platinum crucible (P. 7). By this treatment with boiling H_2SO_4, Al_2O_3 and TiO_2, if present in the residue, are also dissolved in large quantity.

7. If the use of a platinum crucible or of hydrofluoric acid is impracticable, the residue insoluble in HCl and HNO_3 may be fused in a porcelain crucible with a mixture of Na_2CO_3 and K_2CO_3, as described in P. 8, instead of being treated by P. 5—7. This is, however, a far less satisfactory method of analysis, for the following reasons:—Compounds of the alkali elements are used as a flux, and aluminium, calcium, and silica are introduced from the porcelain crucible, so that these elements can-

* From the *Technology Quarterly*, xix., No. 3, September, 1906.

not be tested for in the insoluble residue. Moreover, the treatment with HF and H_2SO_4 is almost always a shorter process, since when the residue consists only of silica, as is often the case with minerals, no further treatment is necessary, and since in other cases there is often no residue to be boiled with Na_2CO_3 solution (P. 6) and seldom one to be fused with Na_2CO_3 (P. 7). A fusion in a platinum crucible with alkali metal carbonate would be less objectionable; but this is not possible unless reducible metallic elements are known to be absent in the residue (see P. 7, N. 1).

Procedure 6.—Transfer the residue insoluble in H_2SO_4 (P. 5) to a casserole, add about 25 cc. saturated Na_2CO_3 solution (see, however, *P 6a, N. 1, if a small quantity of tungsten is to be tested for), cover the casserole, and boil gently for ten minutes. Filter and wash the residue thoroughly. Filtrate, reject or test for tungsten by *P. 6a). Heat the residue with 5 cc. HCl (1·12), measured in a graduate, and 10 cc. water; filter, wash the residue, and treat it by P. 7. Dilute the solution to 40 cc., and treat it with H_2S by P. 21, subsequently testing it only for lead, bismuth, antimony, chromium, barium, strontium, and calcium.

Notes.

1. The boiling with Na_2CO_3 converts into carbonates the sulphates of lead, calcium, strontium, and bismuth completely, and at least 80 per cent of the sulphate of barium, even when large quantities of them are present. A second treatment, which should be applied to the residue if there are indications that barium is present, completely decomposes $BaSO_4$. The carbonates dissolve readily in HCl. Anhydrous chromic sulphate, which is left undissolved by dilute H_2SO_4 (P. 5) as a fine pink or grey powder, is slowly changed by boiling with Na_2CO_3 to a greenish blue hydroxide which dissolves in the HCl, leaving behind the still undecomposed sulphate. Antimonic oxide dissolves only to a small extent (2 to 4 mgrms.) in the Na_2CO_3 solution, but dissolves upon boiling with HCl. Tungstic oxide passes into the Na_2CO_3 solution as sodium tungstate, Na_2WO_4.

2. Any residue insoluble in HCl can therefore consist only of barium and chromic sulphates or of some of the original substance still undecomposed, consisting probably of one of the native oxides or silicates mentioned in P. 5, N. 5. Such a residue will seldom be obtained; and if so, it can ordinarily be rendered soluble by fusion with Na_2CO_3 and KNO_3 (or with KOH) as described in P. 7 (or P. 7, N. 2).

3. The residue undissolved by dilute H_2SO_4 after the treatment with HF (P. 5) is first boiled with Na_2CO_3 solution and not at once fused, since it is necessary to remove the reducible metals—lead, bismuth, and antimony—before a platinum crucible can be used for the fusion. Moreover, the boiling with Na_2CO_3 solution makes subsequent fusion unnecessary when the residue consists only of sulphate of lead or of an alkaline earth element.

**Procedure* 6a.—Acidify the Na_2CO_3 solution (P. 6) with HNO_3, evaporate almost to dryness, add 1 to 2 cc. HNO_3 (1·20); add enough water to dissolve the salt, boil, and cool. (Yellow precipitate, presence of *tungsten*). Filter and wash the precipitate, rejecting the solution. Pour through the filter 2 cc. NH_4OH (0·96) to dissolve any H_2WO_4, acidify the filtrate with HCl (1·20), and add a few granules of zinc. (Blue colour, presence of *tungsten*).

Notes.

1. When HNO_3 is added to a tungstate solution a hydrated tungstic acid separates as a white flocculent precipitate, which changes upon boiling to a yellow powder (H_2WO_4). The test is not very delicate in the presence of a large amount of salt; when 25 cc. Na_2CO_3 solution are used, as is directed in P. 6, even 3 mgrms. of tungsten can barely be detected in this way. Therefore, when tungsten is to be tested for, the residue from P. 5 should first be boiled with a small portion (5 cc.) of Na_2CO_3 solution, and this solution tested for tungsten as described above; under these conditions 1 mgrm. can be detected. The test is entirely unsatisfactory if H_2SO_4 or HCl is used, in place of HNO_3, in neutralising the Na_2CO_3.

2. The blue colour obtained upon reduction with zinc, which serves as a confirmatory test for tungsten, is due to a suspended, quickly coagulating precipitate, consisting of a hydrated oxide intermediate between WO_3 and WO_2. Prolonged action of zinc may cause the blue colour to disappear, owing to complete reduction to WO_2.

3. At this point will usually be found all the tungsten in the substance in excess of 2 mgrms., which amount remains in solution in the H_2SO_4 (P. 5). When, however, phosphate is also present in the substance, tungsten would not remain as H_2WO_4 in P. 3 and 4, but would pass into the acid solution, owing to the formation of a complex phospho-tungstic acid.

Procedure 7.—Transfer the residue insoluble in HCl (P. 6), with the filter if necessary, to a platinum crucible, heat until the residue is dry or until the filter is destroyed, mix the residue with 5 to 10 grms. of anhydrous Na_2CO_3 and 0·1 to 0·5 grm. of solid KNO_3, cover the crucible, and heat over a powerful burner. After some minutes note whether a perfectly fluid fusion has resulted. If not, heat more intensely over a blast-lamp for ten minutes, adding, if necessary, more Na_2CO_3. Cool, place the crucible in a casserole, add carefully HCl (1·12) till the solution remains strongly acid, evaporate to dryness, and heat at 120—130° to render silica insoluble; add from a graduate 4 cc. HCl (1·12) and 10 to 20 cc. water, boil, and filter. Dilute the filtrate to 40 cc., and treat it with H_2S by P. 21, subsequently testing it for all metallic elements except the alkalis. Test the residue for silica by P. 5, and remove it if present; if a residue still remains, treat it as described in N. 3.

Notes.

1. Compounds of the elements of the silver, copper, and tin groups that may be reduced to the metal by heating with an alkaline flux must not be heated in platinum. The same is true of sulphur, sulphides, and in the presence of organic matter of phosphates; for all these elements form easily fusible alloys with the platinum, and thus spoil the crucible. If, however, the substance has been treated by the preceding procedures, none of these substances can be present. Moreover, alkaline hydroxides and strongly oxidising fluxes (such as peroxides and nitrates) must not be fused in platinum, since they attack it fairly rapidly. Therefore, no more nitrate should be added to the Na_2CO_3 fusion than is necessary.

2. In regard to the decomposition of substances in general by fusion with Na_2CO_3, see P. 8, N. 1. Of the substances that may be present in the residue which has been boiled with Na_2CO_3 solution, the silicates are decomposed by fusion with Na_2CO_3 alone. But in order to render chromium compounds (and molybdenum sulphide) soluble, they must be oxidised; and for that purpose a little KNO_3 is added. The native and ignited oxides of tin, aluminium, and titanium are only slowly acted upon by the flux, and remain insoluble with the silica upon the subsequent treatment with acid. $BaSO_4$, if still present, will also remain with the silica; for, though it is converted into $BaCO_3$ and Na_2SO_4 by the fusion, it is formed again when the mass is treated with acid.

3. Any residue insoluble in dilute HCl probably consists, therefore, only of SiO_2, TiO_2, $BaSO_4$, Al_2O_3, and SnO_2. Such a residue is best treated first by P. 5 and 6, to remove SiO_2 and $BaSO_4$, and any residue still remaining may then be treated as follows:—Reduce it to a very fine powder, transfer it to a nickel or silver crucible, dry thoroughly, add 5 to 10 grms. pure solid

KOH, and fuse the mixture for ten to twenty minutes. Cool, extract with about 30 cc. water, and filter. Neutralise the solution exactly with HCl (1·12). Treat the residue with about 5 cc. HCl (1·12), filter out any residue of undecomposed substance, and unite the solution with the neutral aqueous extract. Treat the mixture by the regular procedure beginning with P. 21, testing especially for tin, titanium, and aluminium. The native and ignited oxides of aluminium, stannic tin, and titanium, if finely powdered, dissolve rapidly in fused KOH; and the aqueous extract contains the aluminium as aluminate and most of the tin as stannate. The residue undissolved by water may consist of black nickel oxide from the crucible, stannic hydroxide, potassium titanate, and sometimes other hydroxides accompanying the aluminium or tin oxides. All of these dissolve in HCl.

(To be continued).

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting March 7th, 1907.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MESSRS. Frank Baker, F. S. Benton, L. H. Berry, F. J. Harris, A. T. King, B. D. Porritt, F. G. P. Remfry, A. H. Salway, and Frank Tutin were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Arthur Cunningham, B.A., Presidency College, Calcutta, India; Samuel Duckworth, M.Sc., 78, Alexandra Road, Lowestoft, Suffolk; Arthur George Harrington, Rochford, Westbury Road, Ealing, W.; Frederic William Rixon, M.Sc., Ph.D., Powderham Road, Newton Abbott, Devonshire; William Griffiths Tonner, B.Sc., 26, Gordon Road, Kingston-on-Thames.

The CHAIRMAN read the names of the Fellows recommended by the Council for election as official and ordinary Members of Council, and announced that the name of Mr. F. H. Streatfeild had been proposed by another Fellow as an ordinary Member of Council.

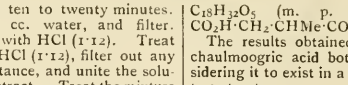
Of the following papers, those marked * were read:—

*30. *The Constitution of Chaulmoogric and Hydnocarpic Acids.*" By MARMADUKE BARROWCLIFF and FREDERICK BELDING POWER.

In previous communications (Power and Gornall, *Trans.*, 1904, lxxxv., 838, 851) the isolation and properties of chaulmoogric acid, $C_{18}H_{32}O_2$ (m. p. 68°) were described. It is optically active, having $[\alpha]_D$ +56°, and was shown to contain both a closed ring and an ethylenic linking.

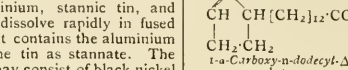
When chaulmoogric acid is oxidised in alkaline solution with limited quantities of potassium permanganate it yields *α-dihydroxydihydrochaulmoogric acid*, $C_{18}H_{32}O_2(OH)_2$ (m. p. 105°; $[\alpha]_D$ +11·6°), *β-dihydroxydihydrochaulmoogric acid*, $C_{18}H_{32}O_2(OH)_2$ (m. p. 93°: $[\alpha]_D$ −14·2°), and *hydroxyketodihydrochaulmoogric acid*, $C_{18}H_{32}O_4$. Further oxidation gives, on the one hand, an optically inactive tricarboxylic acid, $C_{18}H_{32}O_6$ (m. p. 68°), which is *n-pentadecane-aa'γ-tricarboxylic acid*, $CO_2H\cdot[CH_2]_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, and, on the other hand, formic acid and a keto-acid, $C_{17}H_{30}O_5$, previously described (*loc. cit.*), which is now shown to possess the formula $CO_2H\cdot CH_2\cdot CO\cdot[CH_2]_{12}\cdot CO_2H$. The latter compound, on oxidation, yields *n*-dodecanedicarboxylic acid, $[CH_2]_{12}(CO_2H)_2$, and *n*-undecanedicarboxylic acid, $[CH_2]_{11}(CO_2H)_2$. By the addition of hydrogen bromide to chaulmoogric acid, and its subsequent elimination, an optically active mixture of acids is obtained, which, when oxidised, furnishes a keto-acid, $C_{18}H_{32}O_5$ (m. p. 126°), to which the formula, $CO_2H\cdot CH_2\cdot CHMe\cdot CO\cdot[CH_2]_{12}\cdot CO_2H$, is ascribed.

The results obtained can be explained by assigning to chaulmoogric acid both the following formulæ, and considering it to exist in a state of tautomerism between the two structures.

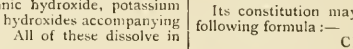


1-α-Carboxy-n-dodecyl-Δ4-cyclopentene. *1-α-Carboxy-n-dodecyl-1:4-bicyclopentane*

Its constitution may therefore be represented by the following formula:—



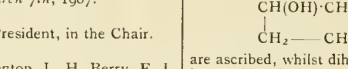
To the dihydroxydihydrochaulmoogric acids the formulæ:



and—

are ascribed, whilst dihydrochaulmoogric acid, $C_{18}H_{34}O_2$, is considered to be a mixture of *α-carboxy-n-dodecylcyclopentane*, and *i-α-carboxy-n-dodecyl-2-methylcyclobutane*.

Hydnocarpic acid, $C_{16}H_{28}O_2$ (m. p. 60°; $[\alpha]_D$ +68°), a homologue of chaulmoogric acid (*Trans.*, 1905, lxxxvii., 884), yielded on oxidation an acid, $C_{16}H_{28}O_6$ (m. p. 60°), which is *n-tridecane-aa'γ-tricarboxylic acid*, $CO_2H\cdot[CH_2]_2\cdot CH(CO_2H)\cdot[CH_2]_{10}\cdot CO_2H$, together with *n*-decanedicarboxylic acid, $[CH_2]_{10}(CO_2H)_2$. Its constitution may accordingly be represented by the following formula:—



*51. "*Hydrolysis of Amygdalin by Acids.*" By ROBERT JOHN CALDWELL and STEPHEN LEWIS COURTAULD.

With the object of obtaining further evidence as to the constitution of amygdalin, the authors have systematically studied the action of acids in comparison with that of enzymes on this "bioside."

The results show that, although amygdalin is ultimately resolved by acids into hydrogen cyanide, benzaldehyde, and two molecular proportions of glucose, the separation of the glucose is effected in two stages. The hydrolysis of the biose section of the molecule proceeds only at about one-sixth of the rate at which maltose is hydrolysed under like conditions. By carefully hydrolysing amygdalin by means of a normal solution of hydrogen chloride at 60°, the authors have prepared the mandelonitrile glucoside which E. Fischer obtained by subjecting the bioside to the action of an extract of yeast; this method of obtaining the glucoside appears to be in some respects advantageous, the product being more easily purified.

*52. "*Mandelonitrile Glucosides. Prulaurasin.*" By ROBERT JOHN CALDWELL and STEPHEN LEWIS COURTAULD.

In order to ascertain whether the glucoside prepared by hydrolysing amygdalin is a direct product or one which has undergone isomeric change, the authors have subjected it to the action of alkalis; they find that it is converted into a substance identical with the isomeric substance prulaurasin, isolated by Hérissey from laurel leaves. Fischer's glucoside therefore bears the same relation to

prulaurasin as amygdalin bears to the *iso*amygdalin described by Dakin, which is to be regarded as the derivative of inactive mandelonitrile, amygdalin and Fischer's glucoside being derived from *l*-mandelonitrile. As the rotatory power of prulaurasin is intermediate between that of Fischer's glucoside and that of sambunigrin, the second isomeride of Fischer's glucoside recently described by Bourquelot and Danjou, the latter must be regarded as the *β*-glucoside of *d*-mandelonitrile.

Characteristic acetyl derivatives have been prepared from amygdalin, *iso*amygdalin, Fischer's glucoside, and prulaurasin.

*53. "*The Hydrolysis of Amygdalin by Emulsin.*" By Samuel James Manson Auld.

Although amygdalin is generally described as the maltoside of benzaldehydecyanohydrin since on hydrolysis it produces two molecules of dextrose, it is probable that the biose residue is an unknown *αβ*-disaccharide capable of hydrolysis both by emulsin and maltase.

The hydrolysis of amygdalin by emulsin may proceed in three ways, depending on the mode of attachment of the emulsin. Either mandelonitrile glucoside and dextrose are first produced with subsequent hydrolysis of the former, or benzaldehydecyanohydrin and the *αβ*-disaccharide are formed, and the latter then resolves into two molecules of dextrose, or, lastly, the amygdalin may undergo fission into the three components by direct abstraction of the dextrose residue attached to the benzaldehydecyanohydrin molecule, The experiments so far carried out indicate that the second process of cleavage is the true one.

Discussion (on the three foregoing papers).

Dr. McKenzie asked whether two mandelonitrile glucosides had been obtained, where the relationship is similar to that which exists between amygdalin and *iso*amygdalin, and, further, if the mandelonitrile glucoside described was racemic as regards the mandelic complex, had the fractional hydrolysis of this compound been studied?

Dr. Henry stated that the report on "Cyanogenesis in Plants," prepared by Professor Dunstan and himself for the York Meeting of the British Association, was mainly a compilation of the published information then available on the subject, and consequently the reference there to amygdalin as a derivative of maltose did not commit the authors of the Report to that view of the constitution of the biose residue of the glucoside and, in fact, the nature of the sugar residue of amygdalin was then under investigation by Dr. Auld, who had been associated recently with the authors in their work on cyanogenetic glucosides.

The interest shown of late in this subject had been created by the work done at the Imperial Institute since 1900, and it had been the intention of Professor Dunstan and himself to investigate fully the relationship of Fischer's mandelonitrile glucoside to prulaurasin and sambunigrin. In view of the fact that Professor Dunstan and he were well known to be at work in this field, it was unfortunate that Messrs. Caldwell and Courtauld had, without consultation, commenced work on these three isomerides.

Dr. Auld regretted that he was not aware that this investigation had been undertaken, as he had been at work on the problem of the constitution of the biose residue of amygdalin for some time. It was an entirely erroneous assumption that the maltose structure of this residue had been taken for granted. Dr. Henry's article in *Science Progress* (July, 1906) clearly showed that the exact nature of the sugar residue in these glucosides had not been settled. The results of Messrs. Caldwell and Courtauld's communication did not throw much new light on the actual configuration of the biose residue.

*54. "*Electrolytic Reduction.*" (Part III.). By Herbert Drake Law.

The products of electrolytic reduction of the aromatic aldehydes in alkaline solution are compounds of the hydrobenzoin type, but this reaction is completely altered when a methyl group is substituted in the ortho- or meta-position of the benzene nucleus. In the latter case, compounds of a resinous nature are obtained. Thus *p*-tolualdehyde gives a well-defined crystalline substance, whilst *m*- and *o*-tolualdehydes yield nothing but resins. The resinifying effect of a single substitution may, however, be neutralised by the introduction of a second group in a similar position on the opposite side of the nucleus. Thus with 3 : 5-dimethylbenzaldehyde a crystalline product is obtained, whilst 2 : 4-dimethylbenzaldehyde yields 40 per cent of resin. Similar results were given by other aldehydes.

In acid solution, the products differed greatly at different temperatures. Thus in cold solutions primary alcohols were obtained to a large extent, but at 40° the product was of the hydrobenzoin type. Stilbenes and saturated hydrocarbons were also obtained.

Discussion.

The President asked whether, in writing the formulæ of the aromatic aldehydes sometimes with the Kekulé benzene ring and at others with the "centric" arrangement of bonds, the author intended to convey the idea that the Kekulé formula represented the benzene molecule as unsaturated, and the "centric" formula as saturated.

Mr. Law, in reply, said that the concentric formula best represents the constitution of the benzene nucleus. The introduction of a strain across the molecule distorts this configuration, the greatest mechanical effect being produced for a substitution in the ortho-position. In the latter case, Kekulé's formula probably nearly represents the state of the molecule. Between these two extremes it is possible that many other forms may exist.

*55. "*New Cerium Salts.*" By Gilbert Thomas Morgan and Edward Cohen.

Although in many cases the cerous salts of carboxylic acids, such as the cinnamate, are insoluble, uncrystallisable substances, it has now been shown that the aromatic sulphonates of this element are usually soluble crystalline compounds resembling the thorium sulphonates previously described by one of the authors (*Abstr.*, 1904, i., 892). A representative series of these cerous sulphonates has been prepared together with several other salts of inorganic and organic acids.

Discussion.

Dr. Power called attention to the formula of cerium oxalate, which Dr. Morgan had referred to as being $Ce_2(C_2O_4)_3.9H_2O$, and stated that an investigation of this salt, conducted some years ago by Mr. Frank Shedden and himself (*Journ. Soc. Chem. Ind.*, 1900, xix., 636) had conclusively shown that it contains 10 molecules of water. It was thus perfectly analogous in composition to the oxalates of lanthanum and didymium, which may be represented by the general formula $R'''_2(C_2O_4)_3.10H_2O$.

Dr. Morgan stated that he had, quite incidentally, represented cerous oxalate as $Ce_2(C_2O_4)_3.9H_2O$, as this appeared to be the accepted formula for this well known salt, and was thus given in current works on pharmacy. He had not noticed Dr. Power's correction which showed that the oxalate was in reality a decahydrate, $Ce_2(C_2O_4)_3.10H_2O$.

56. "*Volume Changes which accompany Transformations in the System* $Na_2S_2O_3 : 5H_2O$." By Harry Medforth Dawson and Colin Gyrth Jackson.

The changes which take place in the system $Na_2S_2O_3 : 5H_2O$ when subjected to certain temperature variations have been investigated by the dilatometric method. Volume temperature curves which indicate the relationship of the various forms of the system were described. At a temperature of 25° the system has been obtained in the following six forms, each characterised by a definite volume:—(1) Primary pentahydrate. (2) secondary pentahydrate, (3) secondary tetrahydrate and saturated solution, (4) primary pentahydrate and saturated solution, (5) secondary monohydrate and saturated solution, (6) liquid.

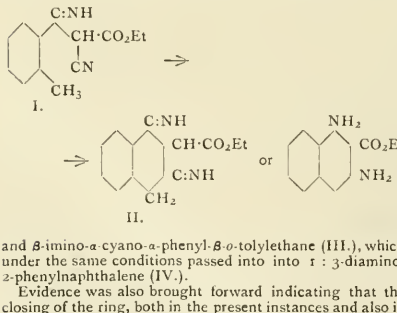
With an accurately calibrated dilatometer the volume occupied by the supercooled liquid of the composition $Na_2S_2O_3 : 5H_2O$ can be directly compared with the volumes of the primary and secondary pentahydrates, and the specific gravities of these obtained with considerable accuracy. The transformation of the metastable secondary pentahydrate into the stable primary form affords an interesting lecture experiment.

57. "*Depression of the Freezing-point of Aqueous Solutions of Hydrogen Peroxide by Potassium Persulphate and other Compounds.*" By THOMAS SLATER PRICE.

Potassium persulphate causes a less molecular depression of the freezing-point of aqueous solutions of hydrogen peroxide than it does of water, and the conclusion is drawn that an unstable compound is formed in solution (compare Friend, *Trans.*, 1906, lxxxix., 1092); similar results hold for potassium sulphate and hydrogen peroxide. In the case of sulphuric acid the molecular depression of hydrogen peroxide solutions is greater than that of water; this confirms the results of Jones and Murray (*Am. Chem. Journ.*, 1903, xxx., 205), that sulphuric acid is dissociated to a greater extent in aqueous hydrogen peroxide than in water. Potassium-hydrogen sulphate and hydrogen peroxide interact in concentrated solution with the production of potassium permonosulphate—no potassium persulphate, $K_2S_2O_8$, is formed—but it was not possible to obtain the pure salt. It was pointed out that a solution of potassium permonosulphate, in the presence of free acid, is much more stable than has been hitherto supposed.

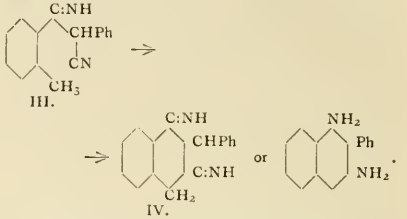
58. "*The Formation and Reactions of Imino-compounds.* Part III. *The Formation of* 1 : 3-*Naphthylenediamine and its Derivatives from* o-*Toluonitrile.*" By ERNEST FRANCIS JOSEPH ATKINSON, HARRY INGHAM, and JOCELYN FIELD THORPE.

In Part II. of this series it was shown that derivatives of benzene containing a saturated side chain of three carbon atoms substituted in the α-position by the nitrile group and in the β-position by the imino-group pass on treatment with cold concentrated sulphuric acid into derivatives of 1 : 3-naphthylenediamine. The authors have now applied this reaction to those derivatives of benzene which possess a saturated side chain of two carbon atoms substituted in the α-position by a nitrile group and in the β-position by an imino-group, and which contain a methyl group in the benzene ring in the ortho-position in respect to the side chain. The two compounds chosen to illustrate this generalisation were ethyl β-imino-α-cyano-β-o-tolylpropionate (I.), which was found to be quantitatively converted into ethyl 1 : 3-naphthylenediamine-2-carboxylate (II.) on being dissolved in cold concentrated sulphuric acid :—



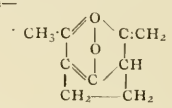
and β-imino-α-cyano-α-phenyl-β-o-tolylethane (III.), which under the same conditions passed into into 1 : 3-diamino-2-phenylnaphthalene (IV.).

Evidence was also brought forward indicating that the closing of the ring, both in the present instances and also in those dealt with in Part II., is due to the formation of a definite addition product formed by the action of concentrated sulphuric acid on the nitrile group.

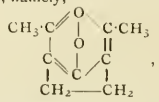


59. "*The Action of Ethylene Dibromide and of Propylene Dibromide on the Disodium Derivative of Diacetylacetone.*" By ALEXANDER WILLIAM BAIN.

By the action of ethylene dibromide on anhydrous disodium diacetylacetone, the author has isolated a *compound* having the formula $C_9H_{16}O_2$, to which he ascribes the constitution—

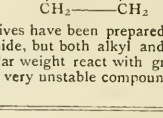


This substance melts at 62—63°, and possesses the remarkable faculty of undergoing isomeric change to a pyrone derivative, namely,—



when heated with concentrated hydrochloric acid. The *hydrochloride* and *platinichloride* of this derivative have been prepared and analysed.

Ammonia reacts with the compound to give—



Similar derivatives have been prepared by the action of propylene dibromide, but both alkyl and alkylene halides of higher molecular weight react with great difficulty and then only to give very unstable compounds.

NOTICES OF BOOKS.

A History of Chemical Theories and Laws. By M. M. PATTISON MUIR, M.A. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

WHILE few students can spare very much time for reading the history of chemistry, it is universally recognised that if they lack definite ideas concerning its development and growth their knowledge cannot but be incomplete, for a good grasp of the science as it now stands can only be obtained by the study of its main achievements in the past. This book provides exactly what the average student requires as a foundation for his reading in the principles of theoretical chemistry. It discusses the history, not of individual substances or groups of substances, but of men's ideas about them, explaining very clearly the errors and false reasonings of earlier days. Long quotations are made from the works of the great masters, and biographical notices are occasionally inserted in which the author con-

trives by his graphic style to convey vivid impressions of the personalities of the men and the value of their work. The book is divided into two main divisions. In the first the growth of knowledge concerning the true nature of a homogeneous substance is traced from the earliest times to the present day, and in the second is described the investigation of correct scientific methods of classifying homogeneous substances, with a view to the discovery of what happens when substances react; in this part the history of the general laws of chemical change is discussed. The physical side of chemistry is treated very scantily, but the author deserves the gratitude of all students whom the spirit of inquiry will not allow to rest satisfied with the statement of definitions and laws without making an endeavour to get at some idea about the process of evolution which modern theories have passed through. By studying this work they will trace the genealogy of the questions which are now stirring in the minds of investigators, and will perhaps be able to form some conception of how their speculations will be answered and what will be the outcome of the development in the future of theories and laws which are now provisionally accepted.

Poisons: their Effects and Detection. By Alexander Wynter Blyth, M.R.C.S., F.I.C., F.C.S., &c., and Meredith Wynter Blyth, B.A. (Cantab), B.Sc. (Lond.), F.I.C., F.C.S., &c. Fourth Edition. London: Charles Griffin and Co., Ltd. 1906.

It would be superfluous to call attention to the special merits of so well known a work as this compendium, and it will be sufficient to point out the alterations and improvements which have been made in the recently issued fourth edition. Descriptions of obsolete and unsatisfactory processes have been deleted to make room for full accounts of the detection, and physiological action of, and symptoms produced by, some poisons, such as sulphonal, which are beginning to come into use, and the section on arsenic has also been much enlarged, fresh methods of identification and determination being described. The chemical constitution of some vegetable poisons is discussed in outline, and the whole book is so thoroughly practical and up to date that toxicologists will find it a most useful and trustworthy guide.

Internal Energy. By John V. V. Bookaem, M.E. New York: McGraw Publishing Company. 1906.

The author of this monograph believes that he has discovered a method of estimating the amount of chemical energy stored within a body. His hypothesis is based upon the measurement of chemical change by expansion through heat, and the measurements were first taken with copper and iron, and were then extended to other metals. It cannot be denied that the calculated results in some cases at any rate show a very good agreement with the values obtained experimentally, but the figures, although they show the main line of the argument, are insufficient to establish the truth of the hypothesis, and the monograph suffers from the disadvantage that the wording is so obscure in places that it is difficult to discern the author's meaning.

Principles and Practice of Agricultural Analysis. Vol. I. *Soils.* By Harvey W. Wiley, A.M., Ph.D. Second Edition. Easton, Pa.: The Chemical Publishing Company. 1906.

The alterations which have been introduced into the second edition of this book are of very considerable importance, and it may almost be said to constitute a new work, preserving, however, the characteristic good features of its predecessor. The arrangement is as systematic as before, and all processes of soil analysis are treated in great detail, mechanical analysis in particular being described very fully. The activity of nitrifying organisms in the soil is treated chiefly from a chemical point of view, and sufficiently full references are given to enable those who wish to go deeper into the subject to map out the necessary course of reading. Some parts of the contents of the first volume in the first edition, which relate more to fertilisers than to soils, are now relegated to the second volume, and new matter is introduced to bring the book up to date. The author has been particularly careful to include all methods of historical or scientific interest even if technically they may be regarded as superseded, with the result that it is conceivable that the agricultural chemist using the book might find it difficult to choose amongst so many methods the one best suited for his purpose, although he would, on the other hand, be guided by the full descriptions which are given of the official methods of soil analysis recognised in the United States.

OBITUARY.

DEATH OF M. BERTHELOT.

We regret to announce the death, at the age of seventy-nine, of probably the most eminent of French men of science, M. Marcelin Berthelot. Virtual founder of the science of thermo-chemistry and one of the most successful pioneers in the great branch of science known as synthetic chemistry, his distinction as a philosopher, as a writer, and as a great citizen contributed to make his name one of the most justly renowned of the Nineteenth Century in France. Of world-wide reputation as a savant, in whom intuition and a critical method seemed ideally balanced for research, he was no mere recluse. The windows of his laboratory were wide open upon the world. No manifestation of the thought of his time was uncongenial to the encyclopædic curiosity of this intimate friend of Renan. The facility of his assimilative faculty recalled indeed that of the great thinkers and men of action of the renaissance who boxed the compass of the knowledge of their time and to whom nothing that concerned human speculation was foreign. Goethe defined the man of genius as he who is fully abreast of his epoch. Judged by this standard, none ever more deserved the name than Marcelin Berthelot. He passed from his laboratory in the College de France to his seat as Senator at the Luxembourg and from a sitting of the French Academy or of the Academy of Medicine to the Ministerial bench at the Chamber always with the same integral mastery of his intelligence, the same philosophically well-classified and ready mind. Once even, as England remembers, he was Minister for Foreign Affairs. His death is more than a national loss. It is a loss for elevated thought and disinterested research all over the world. The mourning will be general.

M. Berthelot died in very dramatic circumstances. His wife had been ill for a year. When he entered her room on the afternoon of Monday last he found her dead. The shock must have overwhelmed him, for he then and there expired.

Marcelin Pierre Eugène Berthelot was the son of a physician, and was born in Paris on October 29, 1827. Educated at the Lycée Henri IV., he had a brilliant career, but though he specially distinguished himself in philosophy, he ultimately devoted his energies to scientific pursuits. At the beginning of 1851 he was appointed *préparateur* to the chemist Balard at the Collège de France, and it was at this period that he formed with Renan, whose humble lodgings were next door to his own, a friendship which only ended with Renan's death. In 1854 he became famous in the chemical world through his doctoral thesis on the combination of glycerin with acids, a continuation of the classical researches of his countryman, Chevreul, on fats. During the nine years which he spent at the Collège de France he was engaged mainly on problems of

synthetic chemistry, and he succeeded in reproducing from their elements a great number of natural bodies—hydrocarbons, alcohols, fats, sugars—as well as in forming many artificial new ones. His results were summed up in "Chimie Organique fondée sur la Synthèse," which was published in 1860, and marks an era in the history of that branch of chemistry. In 1859 he was chosen Professor of Organic Chemistry at the Ecole de Pharmacie, and six years later a Chair of Organic Chemistry was created for him at the Collège de France, which he occupied for the rest of his life. Here he turned to the second branch of study with which his name is specially associated—that of thermochemistry, or the relations between heat and chemical change—and his researches were described in two large volumes, "Mécanique Chimique fondée sur la Thermo-chimie," published in 1879, followed by two more on "Thermo-chimie" in 1897. By a natural extension of these studies he was led to the investigation of explosives from both the theoretical and practical aspects; the former were represented by his book "Sur la Force de la Poudre et des Matières Explosives," published in 1872, and the latter by the services he rendered his country by providing ammunition, devising mines, &c., during the siege of Paris, and later as head of the French Explosives Committee. Later in his life he turned his attention to the history of the science which he so greatly adorned, and his book on "Les Origines de l'Alchimie," together with his publication, with translations and notes, of various old Greek, Arabic, and Syriac treatises on alchemy, shed a flood of light on the chemistry of the Middle Ages. Berthelot, who succeeded Pasteur in 1889 as perpetual secretary of the Academy of Sciences, was Minister of Public Instruction in the Goblet Cabinet in 1886-87, and Minister of Foreign Affairs in the Bourgeois Cabinet in 1895-96. From 1876 he was Inspector-General of Higher Education, and he continued to take a keen interest in educational questions after his election as a life Senator in 1881.—*The Times.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

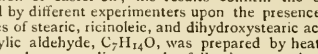
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 9, March 4, 1907.

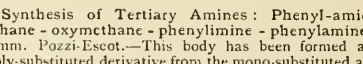
Heats of Combustion and Formation of certain Nitrogenous Bodies of Physiological Value.—M. Berthelot and Ph. Landrieu.—The following results were obtained by combustion with oxygen of specimens of hæmatin, hæmoglobin, and bilirubin:—1. *Hæmatin.*—Fine brilliant crystals, deep violet, losing weight when dried at 115° in a current of dry air. Analysis—C, 64·0; H, 5·1; N, 9·9; Fe, 9·9; O, &c., 11·1. Heat of combustion for 1 grm. substance = 5231 cals. at constant volume, 5236 cals. at constant pressure; the final state being CO_2, H_2O, and magnetic iron oxide, making for 1 grm. C (at constant pressure) 8181 cals. Heat of formation for 1 grm. substance = +1691 cals. 2. *Bilirubin.*—Non-crystalline brown powder. Dried as in the preceding case. Analysis—C, 66·01; H, 6·01; N, 9·03; O, 18·95. Supposed formula, $C_{16}H_{18}N_2O_4$ . . . 302; mean heat of combustion, 6787 at constant volume, 6793 at constant pressure, making, for 1 grm. C, 10,291 cals.; for the formula, 2051·5 cals. Heat of formation for 1 grm., +1505 cals.; for the formula, 454·5 cals. 3. *Hæmoglobin of Horse.*—Brilliant deep red needles. Heat of combustion, 5889 cals. at constant pressure. In 1891 this figure was given as 5914·8 cals., with the analysis—C, 55·48; H, 7·30; N, 17·64; S, 1·11; P, 0·82; O, 17·65. From this the heat of formation is 1091 cals.

Alcoholysis of Castor-oil.—A. Haller.—The author has investigated the bodies resulting from the alcoholysis of castor-oil, when the process is carried out with alcohols containing 1 to 2 per cent of acid. He succeeded in isolating and identifying, in the form of ether-salts of saturated alcohols, the different acids entering into the composition of castor-oil; his results confirm the data furnished by different experimenters upon the presence of glycerides of stearic, ricinoleic, and dihydroxystearic acids. Ænanthylic aldehyde, $C_7H_{14}O$, was prepared by heating ricinoleic ether according to the following equation:— $C_{18}H_{33}O_3R = C_7H_{14}O + C_{11}H_{19}O_2R$.

Synthesis of Tertiary Amines: Phenyl-amido-ethane - oxymethane - phenylimine - phenylamine.—Emm. Pozzi-Escot.—This body has been formed as a poly-substituted derivative from the mono-substituted acid, ethanoic-thiomethane-imine-phenylamine,—



by the action of phenylamine. The resulting compound, consisting of white crystals, fusing at 289°, is represented thus:—



Constitution of Hordenine.—E. Léger.—The formula hitherto ascribed to hordenine is—

$$C_6H_4\begin{cases}CH_2—CH_2—N\begin{cases}CH_3\\CH_3\end{cases}\\OH(4)\end{cases}.$$

The existence of the groups $C_6H_4\begin{cases}\\OH\end{cases}$ and $—N\begin{cases}CH_3\\CH_3\end{cases}$ have been proved beyond dispute, and the object of the present article is to confirm the existence of the chain $—CH_2—CH_2—$ in the para-position to the hydroxyl group. For the experimental proof of this the iodomethylate of methyl hordenine was used. Its formation is given by the following equation:—

$$C_{10}H_{14}N(ONa) + SO_4(CH_3)_2 = C_{10}H_{14}N(OCH_3) + SO_4CH_3Na.$$

One of the decomposition products of this body is the paravinylanisol of hordenine, a heavy liquid hitherto unrecognised. Its identification furnishes the required proof of the presence of the chain $—CH_2—CH_2—$ in the para-position, relatively to the phenol hydroxyl in the molecule of hordenine.

A New Method of Estimating Ammonia in Waters.—Albert Buisson.—The author has previously demonstrated that the estimation of ammonia by the Nessler reagent contains many sources of error, and the method here described, in the first place pointed out by Gerresheim, has now been worked out, and its accuracy verified. Carbonate of soda added to the solution of any salt of ammonia, containing mercuric chloride in the proportion of 5 mols. mercuric chloride to 2 mols. of the ammoniacal salt, causes complete precipitation of the ammonia in the form of a white amorphous compound. This precipitate has been shown to possess a constant composition for slight quantities of ammonia, and has been given the formula $Hg_5N_2Cl_2O + H_2O$, without its having been verified by analysis. It is now found that the simplest formula

possible for this body is $CO_3(Hg_5N_2Cl_2)_2O + 3H_2O$, and the reaction which gives rise to it may be represented thus:—

$$4NH_4Cl + 10HgCl_2 + 10CO_3Na_2 = CO_3(Hg_5N_2Cl_2)_2O + 20NaCl + 9CO_2 + 8H_2O.$$

By this method, quantities of ammonia greater than 1 mgrm. may be estimated with an accuracy at least equal to that of any methods already known.

Method of Synthesis of the Non-substituted β-Ketonic Nitriles.—Ch. Moureu and I. Lazennec.—The acetylene nitriles, $R-C\equiv C-CN$, should, by fixation of water to the acetylene bond, give the β ketonic nitriles, $R-CO-CH_2-CN$. But the authors' attempts at hydration by means of sulphuric acid did not lead to this result. With phenylpropiolic nitrile, $C_6H_5-C\equiv C-CN$, benzoylacetamide, $C_6H_5-CO-CH_2-CONH_2$, was obtained, and amylpropiolic and hexylpropiolic nitriles gave the corresponding acetylene amides, $C_6H_{11}-C\equiv C-CONH_2$ and $C_6H_{13}-C-C\equiv C-CONH_2$. On the other hand, hydrolysis of the products of condensation of the acetylene nitriles with the amines was successfully performed, with formation of the initial amine and the corresponding β ketonic nitrile, *e.g.*,—

$$\underbrace{C_5H_{11}-C=CH-CN \\ | \\ NC_5H_{10}}_{\beta\text{-Amyl-}\beta\text{-piperidylacrylic nitrile}} + H_2O = \underbrace{C_5H_{11}-CO-CH_2-CN}_{\text{Caproilacetonitrile.}} + \underbrace{NHC_5H_{10}}_{\text{Piperidine.}};$$

and this reaction is best carried out with oxalic acid in ethereal solution. This gives a general method of passing from the acetylene nitriles, $R-C\equiv C-CN$, to the corresponding β-ketonic nitriles, $R-CO-CH_2-CN$. The latter are soluble in the aqueous solution of caustic alkalis or alkaline carbonates, from which they are immediately precipitated by acids. The presence of the group CH_2 between the two electro-negative residues CO and CN evidently accounts for the acid character of these compounds.

MISCELLANEOUS.

The Worshipful Company of Goldsmiths has made a donation of £10,000 to the Lawes Agricultural Trust (Rothamsted Experimental Station), to be devoted to research in connection with the soil, and to be known as the Goldsmiths' Company's Fund for Soil Investigation.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Mrs. Ayrton, Mr. S. G. Brown, Mr. W. Duddell, Mr. Horace Duveen, Mr. W. G. Kirkaldy, Mr. J. E. Mounsey, Mr. W. Peacock, Mr. E. H. Rayner, Mr. E. Swash, and Mr. H. Weguelin were elected Members. The Chairman announced the decease of Professor Henri Moissan, Hon. Mem. R.I., on February 20, and of Mr. L. M. Rate, M.R.I., on February 28, and Resolutions of condolence with the families were passed. The Special Thanks of the Members were returned to "A Member" for a Donation of £60, and to Mr. E. R. Merton for his Donation of £50, to the Fund for the Promotion of Experimental Research at Low Temperatures. The following letter from Mr. W. Burdett-Coutts was read:—

1, Stratton Street, W., February 9th, 1907.

Dear Sir,—I have the honour to acknowledge the receipt of your letter of the 8th inst. enclosing a Resolution of the Managers of the Royal Institution of Great Britain with reference to the death of the Baroness Burdett-Coutts. I beg you will assure the Managers of my appreciation of the terms of the Resolution, and my gratitude for the expression of their personal sympathy in the great loss I have sustained. I hope I may be permitted to add a few remarks pertinent to the special bearing of the Resolution, and possibly not uninteresting to the Managers and Members of the Royal Institution. I am perhaps the more entitled to such a privilege in dealing with this important tribute to the Baroness's memory, not so much because I am left by her express desire and act in the position of her sole representative, as by reason of my long and close association with a public life which in its inner aspects was otherwise a singularly solitary one. The Baroness's social relationships to Science, her friendships with many, her acquaintance with nearly all, of its eminent professors for the past seventy years, are well known; her efforts to encourage and aid those who were struggling in the same path, not so well: as was her custom. But it probably is not known—at least to this generation—that, without the equipment of a scientific training, she had the keenest personal interest in Science; she delighted to hear its problems discussed, its discoveries explained; and she never failed to follow, with an attention jealous of apathy or interruption, their learned exposition to those around her. I cannot remember the time when the "man of Science," even one little known at the moment or to the company, had not a special place at her table; or the occasion when her own attention, compelling that of others, did not give him full opportunity. The Baroness was a great educationist. At a time before the State assumed that obligation, she naturally devoted her efforts in that respect to the poorest classes. The later phase of the question still found her in the same field, specialising those efforts in directions which the State has only recently begun to follow. But all the while she was mindful of the claims of science, less popular then than now; and in many ways little known, or not remembered, she brought her ever-watchful eye, her discrimination, and her means, to bear on their advancement. If a scholarship was to be established at Oxford, not classics or history, or even theology, but Science claimed her aid. The great Dr. Routh, notoriously difficult of access in his old age, received her at Magdalen as a young girl, bent on the adventure from a party at Nuneham, and became her friend till he died. Yet even that memory, rich in patristic learning, did not avail to place the Bodleian Library as high in her affections as the University Museum. I would venture the opinion that she believed the Pengelley collection of fossils, rightly studied, would have more practical bearing on future human happiness than a gift of old manuscripts. Such things were not done at haphazard. She would spare no trouble to search out both the need and the means. With a touch of characteristic humour she inquired of Sir Wm. Hooker whether Kew Gardens, so far up the Thames, was not poor in Seaweeds. She had already found out the fact, and had secured the Griffiths collection, so rare and extensive that, without impairing the central completeness, it provided duplicates for six other Botanical establishments. She probably had not read Schimper's monograph on the genus Sphagnum, and did not know the details of the muscological collection of Bruch; but she found out that Kew also wanted Mosses, and that Schimper's great herbarium could be acquired. Thus, not so much by wealth as by thoughtful insight, special departments of British Science were enriched at her hands. I could multiply such instances, if time served, in more local spheres; and extend them to branches of science with which the Royal Institution is more directly concerned. It is almost superfluous to say they would touch the careers of many students of Science, young and old, experimentalists, discoverers, halting in their progress for want of the help that came from an unknown hand. It is not my purpose to examine the motives of this marked and consistent attitude of the Baroness towards Science; rather to suggest, as I believe, that it was in the first place natural, and without motive, satisfying the instincts of a mind peculiarly analytical, suggestive, and acute. But she was also deep-thinking and far-seeing; while she

worked at the daily round, she was looking always to the horizon. She knew the constant and munificent aids that Science had brought, and must continue to bring, to the great human problem to which she devoted her life. And it was inherent in her nature, in days gone by, when Science appealed to a more limited and less generous circle than now, to select it, simply on that account, for such encouragement as her means and position, her personal sympathy and interest, could often afford. I have felt it a grateful duty, to the Baroness's memory, and to the honour paid it by the Royal Institution, to trespass on the Managers' attention at this length, for which I hope the reasons apparent will be adequate excuse.—I am, dear Sir, yours faithfully,

(Signed) W. BURDETT COUTTS.

Sir William Crookes, F.R.S.,
Honorary Secretary, Royal Institution.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2470.

THE THERMAL BEHAVIOUR OF PHOSPHORUS IN ITS COMPOUNDS.

By J. CLARK THOMLINSON, B.Sc.

In dealing with this subject we have hitherto found hydrogen to show a remarkable uniformity of behaviour, the value 7·470 cals. enabling us to show consistent results in demonstrating the existence of thermo-chemical equivalence.

This value can be applied equally satisfactorily in a similar method of treatment of the element phosphorus, in its thermo-chemical relations, for, taking as our starting point gaseous hydrochloric acid, we have the following reaction :—

$$H + Cl = HCl + 22{\cdot}000 \text{ cals.},$$

from which the thermo-chemical equivalent of chlorine would be 22·000 - 7·470 cals. = 14·530 cals.

Although we here bring into notice an element whose thermal value like that of phosphorus we are about to demonstrate, the line of reasoning we are pursuing will be found to confirm such views as we arrive at.

The heats of formation of the tri- and pentachlorides of phosphorus are given in the following equations, from which with the above value for chlorine—

$$P + Cl_3 = PCl_3 + 75{\cdot}300, \quad P + Cl_5 = PCl_5 + 104{\cdot}990 \text{ cals.}$$

we obtain for the element phosphorus as a trivalent element $P\equiv$ = 31·710 cals., and when pentavalent $P\overline{\equiv}$ = 32·340 cals.

For the further treatment of the subject we must recur to the value assigned to oxygen in thermo-chemical reactions.

As a divalent element the value 52·545 cals. for oxygen is applicable to many compounds in which it occurs, and the quadrivalency and pentavalency of oxygen, we found, could be assigned thermal values from a consideration of the heats of formation of hydrogen peroxide and ozone in relation to ordinary oxygen and to the oxides of nitrogen.

Such values for oxygen would be $O\overline{=}$ = 15·180 cals. and $O\overline{\equiv}$ = −3·503 cals. By a simple process of addition which leads us to say that a decrease of two bonds in the valency of oxygen corresponds to an increase of 37·365 cals. in the amount of heat evolved by a grm.-atom of oxygen entering into chemical combination, so we may say that the decrease of one further in the valency of oxygen would correspond to an increase, 18·683 cals., or the thermo-chemical equivalent of oxygen where it exerts only one bond of union in the molecule consistent with its behaviour when di-, quadri-, or pentavalent would be O— = 71·228 cals.

That such a value is consistent with experience may be shown by writing the structural formula for phosphoryl chloride—

where phosphorus is represented as quadrivalent and oxygen presents a univalent character, as described above.

Such a compound, representing phosphorus as quadrivalent, would give to this element an equivalence the mean of 31·710 and 32·340 cals., where the difference is so slight that we can neglect the altered valency of phosphorus in phosphoryl chloride,—

$$PCl_3 + O = POCl_3 + 70{\cdot}660 \text{ cals.}$$

In the above reaction there should be theoretically an evolution of heat equal to 71·228 cals., the agreement of these values confirming the values arrived at above.

The similarity of constitution and association of the acids and acid chlorides of phosphorus at once leads to the following constitutional formula for phosphoric acid :—

which, by calculation, would have the heat of formation 283·298 cals., the actual value being 300·080 cals.

Similarly, the experimental and calculated values for other oxides and acids of phosphorus are—

	Experimental value.	Calculated value
Phosphoric anhydride, P_2O_5 ..	369·900 cals.	327·405 cals.
Phosphorous acid, H_3PO_3 . ..	224·630 „	211·755 „
Hypophosphorous acid, H_3PO_2	137·666 „	159·210 „

In introducing chlorine into the above consideration of the thermochemical equivalent of phosphorus we may also refer to a confirmation of the agreement between theory and experiment as shown in sulphur chloride, S_2Cl_2, and sulphonyl chloride, SO_2Cl_2 (see Chemical News, xciv., p. 152).

With the constitutional formula sulphur chloride resembles hydrogen peroxide, , which has a heat of formation 45·300 cals., the second oxygen atom entering the molecule with an absorption of 23·060 cals., or one-half that given out by a divalent atom when united with both valencies to a monovalent element.

Similarly, divalent sulphur, S= = −9·418 cals., and, as above shown, Cl = 14·530 cals., so that we might expect the heat of formation of sulphur chloride to be represented as the sum of the equivalents of S + Cl^2 and half the heat of formation of a single sulphur atom, this representing the entrance of the second sulphur atom into the molecule, which numerically gives the heat of formation of this compound as 14·933 cals., the experimental value being 14·260 cals.

In the same way sulphonyl chloride, $O\overline{=}S=Cl_2$, gives a calculated heat of formation equal to 87·948 cals., and experiment 89·780 cals.

METHODS FOR THE DETERMINATION OF CREATININ AND CREATIN IN MEATS AND THEIR PRODUCTS.

By H. S. GRINDLEY and H. S. WOODS.

In previous papers from the Chemical Laboratory of the University of Illinois, it has been conclusively proven by improved methods of analysis that meats contain a considerably greater quantity of so-called organic extractives than previous investigations had shown. (See *Journ. Am. Chem. Soc.*, 1904, xxvi., 1086; 1905, xxvii., 658; 1906, xxviii., 25 and 469). It has also been demonstrated that a considerable portion of flesh is soluble in cold water; that the cold water extraction of meat can be made complete, and that it is possible to determine with accuracy the total nitrogenous organic extractives of such extracts. In connection with the researches of this laboratory upon the chemistry of flesh, it became desirable to devise means to ascertain the relative proportion of the different components which go to make up these extractives. The creatin and also the creatinin if present in meats would undoubtedly be completely extracted by cold water. That being true, an attempt was made to apply the colorimetric

method of Folin to the estimation of the creatinin and creatin, using the Duboscq colorimeter (*Zeit. Physiol. Chem.*, 1904, xli., 223; *Am. Journ. Physiol.*, 1905, xiii., 48).

Tests for Creatinin in Meats.

In the first place the method was used to test for creatinin in a cold water extract of chicken flesh. 200 cc. portions of the extract, representing 4·112 grms. of fresh chicken flesh, were tested directly for creatinin in the manner described by Folin in estimating this constituent in urines. The tests gave only the slightest indications, if any, of the presence of creatinin. When the alkaline picrate solution of the extract of the chicken flesh was allowed to stand for a few days it turned red, the colour growing more intense each day. Water extracts of beef and solutions of meat extracts when treated directly with the alkaline picrate solution behaved in a similar manner, showing that creatin under these conditions is gradually converted into creatinin even in alkaline solutions. This is contrary to the supposed behaviour of these two nitrogenous bodies in the presence of alkaline solutions. The true nature of this reaction is now being further studied in this laboratory.

In order to prove further the presence or absence of creatinin in aqueous extracts of fresh flesh, 400 cc. of a cold water extract of beef, representing all of the soluble constituents from 8 grms. of lean beef round, were tested directly for creatinin as above by Folin's method. The tests gave no trace of creatinin. The alkaline picrate solutions of these beef extracts upon standing for a few hours gradually turned red, as did the extracts from chicken flesh. These experiments, which have often been repeated, demonstrate that the work and conclusions of Toppelius and Pommerehne (*Arch. de Pharm.*, 1896, ccxxxiv., 380), and later that of Emil Wörner (*Zeit. Physiol. Chem.*, 1899, xxvii., 1), were correct, and that the investigations of G. S. Johnson (*Proc. Roy. Soc.*, 1901, l., 287), which led him to the deductions that perfectly fresh meats contain creatinin, but no creatin, were wrong. As judged by Jaffe's reaction fresh meats contain only the slightest trace of creatinin if any at all. However, the creatin of flesh is, in part at least, very readily changed to creatinin. The following experiment demonstrates this fact:— Three 500 cc. portions of a cold water extract, each representing 10·015 grms. of chicken flesh, were carefully evaporated upon a water-bath to a volume of 50 cc. in order to completely coagulate the soluble proteid matter. The solutions were filtered, the precipitates thoroughly washed, and the filtrates evaporated to a volume of 75 cc. They were then tested for creatinin and they gave readings which represented 0·08, 0·11, and 0·15 per cent of creatin, calculated upon the basis of the fresh substance of the flesh. This experiment and a number of others which we have made prove that the evaporation of an aqueous extract of flesh upon the water-bath, in the presence of its natural acidity, changes creatin to creatinin. It is just possible that this action may be one influence which produces flavour during the cooking of meats. This subject is now being studied in connection with these researches.

Estimation of Creatin in Meats.

The estimation of creatin in the aqueous extracts of flesh were made by taking 500 cc. portions of the solution, evaporating and filtering as mentioned above to remove the coagulable proteids. The solutions thus obtained were treated with hydrochloric acid and evaporated upon the water-bath to a small volume. This treatment was repeated with the addition of water until all the creatin had been changed to creatinin. The solutions were then made up to exactly 100 cc. and 30, 40, and 50 cc. of the same were used to make the quantitative test with the colorimeter.

Table I. gives a few determinations of creatin in different kinds of flesh.

As a result of the preliminary experiments here reported, the following method is recommended for the estimation of creatin in flesh. Prepare the aqueous extract of the flesh as described in a former paper from this laboratory (*Journ. Am. Chem. Soc.*, 1905, xxvii., 658):—

Evaporate 500 cc. portions of the extracts to 50 cc., filter, wash the coagulated proteid thoroughly with hot water, add 25 cc. of N/10 hydrochloric acid, to each of the filtrates, and evaporate them to a volume of 10 to 15 cc. Now add 50 cc. of water and 10 cc. of N/10 hydrochloric acid and again evaporate to a volume of 10 to 15 cc. Care must be taken to insure the complete change of creatin to creatinin. Cool the solutions, transfer them to a 100 cc. measuring flask, and dilute to the mark. Transfer an aliquot portion of this latter solution, equivalent to 200 cc. of the original extract, to a 500 cc. flask, add 15 cc. of a 1·2 per cent (saturated) picric acid solution and 5 cc. of a 10 per cent sodium hydroxide solution, shake well, and allow the solution to stand for five minutes. In the meantime practice reading the colorimeter, using an N/2 solution of potassium bichromate in each cylinder. Now dilute the alkaline creatinin picrate solution to 500 cc., mix thoroughly, rinse one of the cylinders well with this unknown solution, add a portion of the solution to the cylinder, and make several careful readings at once, comparing the unknown solution with 8·0 mm. of the bichromate solution. According to Folin, the correct reading in millimetres divided into 81 gives the number of milligrms. of creatinin present. This figure multiplied by 1·16 gives the number of milligrms. of creatin. If an aliquot portion equivalent to 200 cc. of the extract does not give a satisfactory reading, use such a portion as will give a reading of about 8 mm.

This method has been used successfully for the determination of creatinin and creatin in uncooked and cooked meats and in meat broths and meat drippings.

Creatinin and Creatin of Commercial Beef Extracts.

(Note.—After the data herein recorded had been obtained, and this paper had been written, the number of the *Journal of the American Chemical Society* for October, 1906, was received containing the paper of Bigelow and Cook upon "The Separation of Proteoses and Peptones from the simpler Amino-bodies." In this paper the authors mention the fact that they have applied the method of Folin for the determination of creatin in meat extracts, but they give no analytical results. Notwithstanding this preliminary notice of Bigelow and Cook it was deemed advisable to publish our paper in full and without any modifications, since it gives data which prove without doubt that the method of Folin may be applied successfully to the estimation of creatinin and creatin in meats, in meat broths, in meat extracts, and in other meat products. We have been using this method continuously in our investigations upon the chemistry of flesh since March 15, 1906).

The nature of a considerable proportion of the constituents of commercial beef extracts is still unknown. A ready method for the estimation of creatinin and creatin in these products would undoubtedly be useful in determining the commercial value and the grade of the various commercial beef extracts and similar preparations which are now upon the market. As Folin's method for the estimation of these substances in urines proved to be an excellent means for the determination of these nitrogenous constituents which are contained in aqueous extracts of flesh, we undertook to apply it to the determination of these bodies in commercial extracts. The method has proved equally successful in this connection. Its application here has demonstrated that commercial beef extracts contain both creatinin and creatin. The details of the procedure in the case of the extracts are entirely similar to those outlined above for cold water extracts of flesh. The results of a number of determinations of creatinin and creatin in a number of the prominent commercial extracts now on the market are given in Tables II., III., and IV.

These results show that there are marked differences in commercial meat extracts as to their content of creatinin

Table I.—*Creatin in Fresh Flesh.*

No. of sample.	Kind of meat.	Weight of sample.	Reading of colorimeter.	Weight of creatinin due to creatin (A).	Weight of creatin (A × 1·16).	Creatin.
		Grms.	Mm.	Mgrms.	Mgrms.	Per cent.
2075	Beef round	2·8966	8·2	9·88	11·46	0·41
2084	Cold storage fish.. ..	3·8369	7·9	10·25	11·89	0·31
2085	,, ,, ...	4·6625	7·8	10·38	12·04	0·26
2110	Refrigerated chicken ..	4·0084	8·1	10·00	11·60	0·29
2111	,, ,, ..	4·9152	8·4	9·64	11·18	0·23
2112	,, ,, ..	5·0262	7·8	10·38	12·04	0·24

Table II.—*Creatinin in Commercial Beef Extracts.*

No. of sample.	Weight of sample.	Reading of colorimeter.	Weight of creatinin.	Per cent of creatinin
	Grm.	Mm.	Mgrms.	
1.	0·3008	7·9	10·38	3·45
2.	0·2545	8·6	9·42	3·70
3.	0·5800	8·1	10·00	1·72
4.	0·7221	8·0	10·13	1·40
5.	0·1972	7·8	10·38	5·27
6.	0·7234	8·2	9·88	1·37
7.	0·8206	8·2	9·88	1·20
8.	0·5458	7·7	10·52	1·93
9.	1·1391	8·6	9·42	0·83
10.	0·4720	8·1	10·00	2·12
11.	0·6786	8·5	9·47	1·39
12.	0·7540	7·5	10·08	1·30
13.	0·2774	7·3	11·10	4·00

Table III.—*Creatin in Commercial Beef Extracts.*

No. of sample.	Weight of sample.	Reading of colorimeter	Weight of original creatinin *plus* creatinin due to creatin.	Weight of original creatinin (see Table I.).	Weight of creatinin due to creatin (A).	Weight of creatin (A × 1·16).	Creatin.
	Grm.	Mm.	Mgrms.	Mgrms.	Mgrms.	Mgrms.	Per cent.
2.	0·1833	7·9	10·25	6·78	3·47	4·03	2·18
3.	0·2636	7·7	10·52	4·55	5·97	6·93	2·63
4.	0·1850	7·9	10·25	2·60	7·65	8·74	4·79
5.	0·1512	8·4	9·64	7·96	1·68	1·95	1·29
6.	0·1841	8·6	9·42	2·38	7·04	8·17	4·35
7.	0·1641	8·0	10·13	1·98	8·15	9·45	1·20
8.	0·2593	8·0	10·13	5·00	5·13	5·95	2·29
9.	0·7088	8·8	9·20	5·86	3·34	3·87	0·55
11.	0·3016	5·0	16·20	4·19	12·01	13·93	4·62
12.	0·2262	6·85	11·82	2·91	8·88	10·30	4·55
13.	0·2080	7·00	11·57	8·32	3·25	3·77	1·81

Table IV.—*Combined Creatinin and Creatin in Commercial Beef Extracts.*

No. of sample.	Creatinin.	Creatin.	Sum of creatinin and creatin
	Per cent.	Per cent.	Per cent.
2.	3·70	2·18	5·88
3.	1·72	2·63	4·35
4.	1·40	4·79	6·19
5.	5·27	1·29	6·56
6.	1·37	4·35	5·72
7.	1·20	1·20	2·40
8.	1·93	2·29	4·22
9.	0·83	0·55	1·38
11.	1·39	4·62	6·01
12.	1·30	4·55	5·85
13.	4·00	1·81	5·81

and creatin. In some of the extracts creatinin occurs in considerably greater quantities than does creatin, while in others the amounts of the latter constituent are greater than the amounts of the former. It is difficult to state at present the cause or causes which, in the preparation or keeping of the commercial extracts, produce this variation in the proportion of these two nitrogenous constituents. Experiments upon meat extracts prepared upon a small scale in the laboratory, from fresh meat, are now under way to find out if possible the conditions which produce the above difference in the relative proportion of creatinin and creatin.

The data here given also show that there is a marked difference in the total amount of creatinin and creatin contained in different commercial extracts now upon the market. Further study will probably show that this difference in the combined amount of these nitrogenous constituents is due, in the main, to the material from which they are manufactured. We hope to be able to study this phase of the work in the near future.

We wish here to express our thanks to Mr. H. H. Mitchell for his valuable assistance in connection with the analytical work involved in this paper.—*Journal of Biological Chemistry*, ii., No. 4.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 138).

Procedures and Notes (continued).

Procedure 8.—If the use of HF (P. 5) is impracticable, transfer the residue insoluble in acids (P. 2 or 4), with the filter if necessary, to a porcelain crucible, heat until the residue is dry or until the filter is destroyed, mix the residue, which must be very finely divided, with ten to twenty times its weight of a mixture of anhydrous Na_2CO_3 and K_2CO_3, cover the crucible, heat strongly over a powerful burner or over a blast lamp so that complete fusion takes place, and continue the heating for 10—30 minutes. If dark particles of undecomposed substance can still be seen, add gradually in small portions 0·1—0·5 grm. of solid KNO_3, and heat strongly for several minutes. Cool, boil the crucible and its contents with water until the fused mass is disintegrated, filter, and wash the residue thoroughly. Warm the residue with HNO_3 (1·20) until action ceases, and filter out any still undecomposed substance (see N. 2 below). Mix a small part of the HNO_3 solution with a small part of the Na_2CO_3 solution, making the mixture strongly acid with HNO_3, if it is not already so.

If no precipitate forms, mix the remainder of the acid solution with about half the Na_2CO_3 solution, reserving the rest of the Na_2CO_3 solution for the tests for acid radicals. Add about 5 cc. HCl (1·12) (or more if the solution is still alkaline), and filter. (Precipitate, test for silver and lead, P. 12). Evaporate the solution to dryness, moisten the residue with HCl, and again evaporate to decompose nitrates. Heat the residue until it is thoroughly dry at 120—130° in a hot closet or by keeping it in motion over a small flame. Add from a graduate 4 cc. HCl (1·12) and about 20 cc. water; heat to boiling, filter, reject the residue, and dilute the filtrate to 40 cc. (Filtrate P. 21).

If a precipitate forms on mixing small portions of the HNO_3 solution and the Na_2CO_3 solution, treat these solutions separately as described in the preceding paragraph, uniting the precipitates formed by the same group reagent in the subsequent analysis.

Notes.

1. Upon fusion with Na_2CO_3 most compounds undergo metathesis, the acid radical of the compound combining with the sodium, and the metallic element with the carbonate radical. The carbonate formed is, however, sometimes decomposed by heat with production of the oxide or of the metal itself. Acid-forming oxides, such as SiO_2, As_2O_5, and less rapidly Al_2O_3, expel CO_2 from the Na_2CO_3 and form sodium salts. Such reactions are illustrated by the following equations:—

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$
$$Fe_2SiO_5 + Na_2CO_3 = Na_2SiO_3 + Fe_2O_3 + CO_2.$$
$$4AgCl + 2Na_2CO_3 = 4NaCl + 4Ag + 2CO_2 \uparrow + O_2.$$
$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2.$$

After the treatment with water, the acid radical of the substance is therefore found with the excess of Na_2CO_3 in the aqueous extract, while the metallic component remains undissolved by the water and passes into the acid solution.

2. Some substances which are not much acted upon by Na_2CO_3 alone are readily attacked when an oxidising flux like KNO_3 is present. Thus sulphides are converted into sulphates and chromium compounds (such as chromite, $FeO.Cr_2O_3$) into chromates. A few substances, however, such as the oxides of tin, aluminium, and titanium, may be only partially decomposed even by long-continued fusion with the mixed fluxes. An undecomposed residue is best fused with KOH in a nickel or silver crucible and the fusion treated, as described in P. 7, N. 3, first with water and then with HCl.

3. The porcelain crucible is so attacked by the flux that it cannot well be used for a second fusion. Aluminium, calcium, and silica are taken up by the flux, so that these elements, as well as the alkali elements, cannot be tested for later in the analysis. In case all reducible metallic elements and sulphides are known to be absent (see P. 7, N. 1), it is therefore better to make the fusion in a platinum crucible, since then no foreign substances are introduced from the crucible. If platinum is not available, or if it is not known that reducible elements are absent, a pure nickel crucible can be used with advantage in place of the porcelain one. This enables aluminium, calcium, and silica to be tested for; some nickel, but only a few mgrms., will then be found in the acid solution of the fusion. Reducible elements, if present, would alloy with the nickel, but the destruction of a crucible of this cheap material is not of much consequence. Ordinarily a nickel crucible can be used repeatedly.

4. The first and third reactions given in N. 1 are examples of cases where the aqueous and acid solutions must not be mixed, for upon mixing $BaSO_4$ or AgCl would again be formed.

5. Of the metallic elements that may be present, all or a part of the arsenic, antimony, tin, molybdenum, tungsten, aluminium, chromium, and manganese are contained in the Na_2CO_3 solution; and this solution must therefore be analysed for metallic elements. Since this solution may also contain Na_2SiO_3, the solution after the addition of HCl is evaporated to dryness, and the residue is heated at 120—130°; this treatment partially dehydrates the silicic acid and renders it insoluble in HCl. The residue insoluble in HCl after this treatment usually consists only of silicic acid (or tungstic acid). To prove whether it consists wholly of silica, it may be treated with H_2SO_4 and HF as described in P. 5. *To test for tungsten it may be treated with HCl and zinc as described in *P. 6a.*

6. The residue left after the extraction with water is treated with HNO_3 rather than with HCl, so as to dissolve reduced metals and to prevent the formation of AgCl and $PbCl_2$ at this point.

Confirmatory Experiments and References.

P. 2, N. 1: *Destruction of Organic Matter.*—3 grms. white flour, 1·5 grms. glycerin, 0·5 grm. paraffin, and some filter-paper were treated in separate experiments, according to the procedure: nearly all the organic matter was decomposed by the first two or three treatments with H_2SO_4 and HNO_3, and after a few more treatments colourless solutions were obtained.

P. 2, N. 2.—See C. E., P. 5, N. 4 and 5.

P. 3, N. 7: *Oxidation of Mercurous Salts by* HNO_3.—100 mgrms. Hg as $Hg_2(NO_3)_2$ were boiled with a little HNO_3 (1·42) for one minute, the solution was diluted, and HCl added; no precipitate was formed, thus showing that the mercurous salts had been completely oxidised. 100 mgrms. Hg as $Hg_2(NO_3)_2$ were boiled for ten minutes with 25 cc. HNO_3 (1·04), and HCl was added: a large precipitate of Hg_2Cl_2 resulted, showing that dilute HNO_3 does not oxidise a mercurous salt rapidly.

Volatility of Mercury and Arsenic Compounds.—Separate solutions containing 1 mgrm. Hg as $HgCl_2$ in HNO_3, HCl, *aqua regia*, and H_2SO_4 were carefully evaporated just to dryness; the residue was in each case dissolved in a little water, and the solution saturated with H_2S; a precipitate of HgS estimated by comparison at not less than $\frac{3}{4}$ mgrm. Hg was obtained in each case, showing that not much of the mercury had been volatilised. It was found that $HgCl_2$ was not converted into $Hg(NO_3)_2$ by the evaporation with HNO_3.

1 mgrm. Hg as $HgCl_2$ was heated in a hot closet at 125°, the casserole was washed out with water, and the solution

* From the *Technology Quarterly*, xix., No. 3 September, 1906.

saturated with H_2S: no precipitate was obtained, thus showing that the $HgCl_2$ was completely volatilised.

1 mgrm. Hg as $Hg(NO_3)_2$ was heated for two days at 125° in a hot closet, dissolved in water, and treated with H_2S: an H_2S precipitate resulted, whose size indicated that little or none had volatilised.

10 mgrms. As as As_2O_3 were added to 10 cc. HCl (1·20), and the solution was boiled vigorously for about 15 seconds; the solution was somewhat diluted and then saturated with H_2S: only 1—2 mgrms. As as As_2S_3 were precipitated.

The experiment was repeated, except that the HCl solution was evaporated to 2 cc.: scarcely any precipitate of As_2S_3 was obtained. In another experiment the solution was evaporated to dryness: no precipitate of As_2S_3 formed.

A solution of 10 mgrms. As as As_2O_3 in 10 cc. H_2O and 2 cc. HCl (1·20) was boiled for 30 seconds and H_2S was passed in: a precipitate appearing like that given directly by 10 mgrms. As was obtained, showing that very little if any arsenic was volatilised. A similar solution of 10 mgrms. As was evaporated to 2 cc.; it gave with H_2S a precipitate estimated to contain 3 mgrms. As.

1 and 10 mgrms. As as As_2O_3 dissolved in 5—10 cc. HCl (1·20) were boiled in covered casseroles, oxidised with bromine water, evaporated to dryness, and dissolved in HCl; the solution was then precipitated with H_2S: the amount of arsenic precipitated was estimated to be nearly as great as that originally taken, thus showing that arsenic in the higher state of oxidation is not volatilised.

P. 3, N. 9—12: *Solubility of the Dehydrated Hydroxides in* HNO_3.—For this and for a statement as to other substances that the residue may contain, see A. A. Noyes, *Technology Quarterly*, 1903, xvi., p. 121; also Chemical News, xciii., p. 171.

P. 4, N. 1: *Solubility of* $PbSO_4$, $BaSO_4$, AgCl, *and* $Sn(PO_4)_4$ *in* HCl.—See *Ibid.*, 1903, xvi., p. 126.

Action of HCl *and* HNO_3 *on* AgCN *and* Ag1.—50 mgrms. Ag as freshly precipitated AgCN were boiled with 20—30 cc. HCl (1·20): the precipitate dissolved quickly.

To 50 mgrms. Ag as freshly precipitated AgI were added 10 cc. HNO_3 (1·42), and the mixture was evaporated, diluted, filtered, and HCl was added to the filtrate: a precipitate of AgCl estimated to contain 15 mgrms. Ag was obtained, showing that AgI is slowly decomposed by HNO_3. The experiment was repeated with 50 mgrms. Ag as AgCN: no precipitate of AgCl was obtained.

P. 4, N. 4: *Solubility of Metastannic and Antimonic Acids in* H_2SO_4 *and* HCl.—200 and 400 mgrms. Sn as metastannic acid, which had been heated for one hour in a hot closet at 120°, were treated in separate experiments with 3 cc. concentrated H_2SO_4 as described in the Note: in the first case all the tin, in the second all but a few mgrms. of it, dissolved on boiling the acid for about a minute. The solutions were diluted with 2—3 cc. water and boiled: no precipitate formed. The first solution was cooled and poured into 10 cc. cold water: a solution which remained clear for several hours was obtained, from which a white precipitate separated at once on boiling. To the other solution (containing 400 mgrms. Sn) were added 5 cc. HCl (1·12) and 50 cc. water; no precipitate appeared, even on boiling. The solution was diluted to 200 cc.: a white precipitate then formed, The precipitates obtained from these solutions dissolved readily in dilute HCl and in concentrated H_2SO_4.

200 mgrms. Sb as hydrated Sb_2O_5, previously heated at 120°, were boiled with 5 cc. HCl (1·12) for two or three minutes: complete solution resulted.

200 mgrms. Sb as hydrated Sb_2O_5 did not dissolve in 3 cc. boiling concentrated H_2SO_4 or on dilution, but dissolved readily when HCl was added as described in the Note. This solution was diluted with 10 cc. water: a slight precipitate formed, which dissolved on the addition of a little HCl and warming.

In another experiment 200 mgrms. Sn as dehydrated metastannic acid were boiled for about 30 minutes with HCl (1·20): at the end of that time the solid had dissolved nearly, but not quite completely.

(To be continued).

PHOSPHORIC ACID, POTASH, NITROGEN, SOILS, ASH, AND INSECTICIDES.*

Report of Committee A on Recommendations of Referees.—(R. J. Davidson, *Chairman*).

1. Nitrogen.

It is recommended—

1. That the work on the Fuller modification of the official Gunning method be discontinued, and that the Gunning method remain as it is now stated.

Adopted.

(The Fuller modification consists in the addition of 0·5 to 0·75 grm. of copper sulphate after digesting with sulphuric acid and potassium sulphate for one-half hour).

2. (*a*) That the work on the neutral permanganate method be continued along the same lines as this year, having in mind the influence of excessive amounts of non-nitrogenous material in the source of nitrogen. (*b*) That work be directed along the line of eliminating some of the many details of the method which influence to too great a degree the results obtained.

Adopted.

3. That the work on the alkaline permanganate method be continued, and that the quantity of material taken be changed to 0·0675 grm. nitrogen; that the quantity of alkaline permanganate used in digestion be changed to 150 cc., and that 100 cc. be distilled off before titration. The modified method should read:—

Weigh out an amount of sample containing 0·0675 grm. of nitrogen and transfer to a 600 cc. distilling flask. After connecting with condenser to which the receiver containing the standard acid has been attached, digest with 150 cc. of alkaline permanganate solution (16 grms. of pure potassium permanganate and 150 grms. of sodium hydrate dissolved in water, and made to 1000 cc.) for thirty minutes below the boiling-point. Then boil until 100 cc. of distillate is obtained. If the material shows a tendency to adhere to the sides of the flask an occasional gentle rotation is necessary during distillation.

Referred to the Referee for 1907 for investigation as to whether this method, or some modification of it, can be applied to all organic nitrogenous materials, especially cotton-seed meal.

4. That the method for standardising hydrochloric acid proposed in 1905, and referred to the Referee for 1906, be adopted, and that the method now given in the official methods be dropped. (See *Bull.* 46, Rev., p. 13, under "4—Determination of Nitrogen"). The proposed method reads as follows:—

By means of a preliminary test with silver nitrate solution, to be measured from a burette, with excess of calcium carbonate to neutralise free acid and potassium chromate as indicator, determine exactly the amount of nitrate required to precipitate all the hydrochloric acid. To a measured and also weighed portion of the standard acid add from a burette one drop more of silver-nitrate solution than is required to precipitate the hydrochloric acid. Heat to boiling, cover from the light, and allow to stand until the precipitate is granular. Then wash with hot water through a Gooch crucible, testing the filtrate to prove excess of silver nitrate. Dry the silver chloride at 140° to 150° C.

Adopted as the official method.

* Extracts from the Proceedings of the American Association o Official Agricultural Chemists, 1906.

[*Note by the Secretary.*—The following method for the estimation of nitrogen was submitted by Mr. T. S. Gladding, together with comparative results on 81 samples obtained by the three methods compared, the question being raised as to whether a combination of two official methods, the Gunning and the Kjeldahl, would be considered an official method. Mr. Gladding requested that appropriate action be taken, and the method is submitted for the information of the Referee without instructions from the Association :—

Combination Method : Kjeldahl and Gunning Methods.

One grm. of fertiliser, 25 cc. of sulphuric acid, 10 grms. of potassium sulphate, 0·7 grm. of mercuric oxide ; heat till water white. Cool, add 200 cc. of water, 0·5 grm. of zinc-dust, 25 cc. of potassium sulphide solution, 50 cc. of soda solution, and distil].

2. SEPARATION OF NITROGENOUS BODIES.

A. *Milk and Cheese Proteids.*

It is recommended—

1. That the original method of preparing the water extract (cheese analysis), proposed by Van Slyke and Hart, be so altered as to call for the use of 1000 cc. of water in place of 500 cc. (Proceedings, 1902, *Bull.* 73, p. 89).

Adopted.

2. That the method of drawing the water extract through a thick pad of asbestos, after it has been separated from the fat and insoluble nitrogenous matter by cotton-wool, be further studied.

Adopted.

3. That the temperature at which the extraction is made be further studied.

Adopted.

4. That the completeness of the extraction of matter soluble in salt solution be further studied.

Adopted.

B. *Vegetable Proteids.*

The report of the Referee was received too late for action to be taken by Committee A, but the following recommendation is submitted as a matter of record :—

It is recommended for the purpose of securing greater uniformity of results, that in the extraction of alcohol-soluble nitrogen in wheat and flour 70 per cent alcohol by weight, sp. gr. 0·871, be used.

C. *Meat Proteids.*

It is recommended—

1. That the modified tannin salt method as described in the Proceedings of the Association for 1905 (Bureau of Chemistry, *Bulletin* No. 99, p. 182) be adopted as a provisional method.

Referred again to the Referee for recommendation in 1907.

2. That the xanthin base method of Schittenhelm (Proceedings, 1904, *Chemistry Bull.* No. 90, p. 129) be adopted as a provisional method.

Referred again to the Referee for recommendation in 1907.

3. That the application of the creatinin method as applied by Folin to the urine be further studied by the Association (*Zeit. Phys. Chem.*, 1886, x., 391).

Adopted.

3. INORGANIC PLANT CONSTITUENTS.

It is recommended—

That the peroxide method for total sulphur be adopted as official.

(This method was recommended as provisional by the Referee in 1905, *Bull.* No. 99, p. 133, the following restatement of the method varying only in technique) :—

Peroxide Method for Sulphur in Plants.

Place from 1·5 to 2·5 grms. of material in a nickel crucible of about 100 cc. capacity, and moisten with approximately 2 cc. of water. Mix thoroughly, using a nickel or platinum rod. Add 5 grms. of pure anhydrous sodium carbonate, and mix. Add pure sodium peroxide, small amounts (approximately 0·50 grm.) at a time, thoroughly mixing the charge after each addition. Continue adding the peroxide until the mixture becomes nearly dry and quite granular, requiring usually about 5 grms. of peroxide. Place the crucible over a low alcohol flame (or other flame free from sulphur), and carefully heat with occasional stirring until contents are fused. (Should the material ignite, the determination is worthless). After fusion remove the crucible, allow to cool somewhat, and cover the hardened mass with peroxide to a depth of about 0·5 cm. Heat gradually, and finally with full flame until complete fusion takes place, rotating the crucible from time to time in order to bring any particles adhering to the sides into contact with the oxidising material. Allow to remain over the lamp for ten minutes after fusion is complete. Cool somewhat. Place warm crucible and contents in a 600 cc. beaker, and carefully add about 100 cc. of water. After violent action has ceased, wash material out of crucible, make slightly acid with hydrochloric acid (adding small portions at a time), transfer to a 500 cc. flask, cool, and make to volume. Filter, and take a 200 cc. aliquot for determination of sulphates by precipitating with barium chloride in the usual manner.

Referred to Referee for 1907 for recommendation as to final action.

2. That the combustion method (*i.e.*, the Sauer-Tollens-Barlow method) for determining volatile inorganic plant constituents be further investigated (Sauer, *Zeit. Anal. Chem.*, 1873, xii., 32 ; Barlow-Tollens, *Journ. Am. Chem. Soc.*, 1904, xxvi., 341).

4. POTASH.

It is recommended—

1. That the study of the volumetric method for use in both soil and fertiliser analysis be continued. (Proceedings, 1905, Bureau of Chemistry, *Bull.* No. 99, p. 135).

Adopted.

2. The following recommendation, made by Mr. Cushman, was referred to Committee A after their report had been made. The Committee, however, consider the recommendation subsequent to the adjournment and referred it to the Referee on potash for investigation.

I recommend that the Referee direct his attention to a study of what really constitutes available potash in soils, fertilisers, and ground-mineral products, so that, if possible, we may have a definition of available potash. The Referee, I understand, according to the precedents and rules of our Association, has the right to call in sub-referees, or at least other members of the Association, to aid him in making his report. If there were any machinery for doing it in the Association I think the matter so important that I would suggest the appointment of a representative Committee to study the question carefully ; but as it is I put it in the form of a recommendation that the Referee turn his attention to a definition of available potash.

5. SOILS.

It is recommended—

1. That the fifth-normal nitric-acid digestion method be further studied. (*Bull.* No. 46, p. 74, Sec. *i*, using nitric instead of hydrochloric acid, and digesting at 20° C. instead of 40° C.).

Adopted.

2. That the sodium peroxide fusion method for total phosphorus be given a further trial, and that this be compared with the alkali-carbonate fusion method. (Proceedings, 1905, *Bull.* 99, p. 111 ; details slightly modified in 1906 report).

Adopted.

3. That the modified J. Lawrence Smith method for total potassium, presented at this meeting, be further tested.

Adopted.

This method reads as follows:—The well known ammonium-chloride and calcium-carbonate fusion devised by J. Lawrence Smith is used (Fresenius, "Quantitative Analysis," p. 426). The fused mass is transferred to a porcelain dish, slaked with hot water, finely ground with an agate pestle, and transferred to a filter. After washing free of chlorides the filtrate and washings are concentrated in a Jena beaker to about 20 cc. Filtrate and washings are slightly acidified with hydrochloric acid, concentrated in a platinum dish, and 1½ cc. of a platinic-chloride solution (10 cc. contains 1 grm. of platinum) added where 1 grm. of soil has been used. This is then evaporated to a syrupy consistency as usual, and washed with 80 per cent alcohol and ammonium-chloride solution.

4. That line 30, under "1—Preparation of Sample," p. 71, *Bull.* No. 46, be changed from "openings ¼ millimetre in diameter," to "openings 1 millimetre in diameter," and that "passed through a sieve of 1 millimetre mesh," be omitted from line 1 under (*h*), p. 74.

This change in an official method having been before the Association in 1905, was adopted.

5. That for "3—Determination of Volatile Matter," *Bull.* No. 46, p. 72, substitute the Determination of Total Organic Carbon (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1640) as the official method.

Recommended for adoption as official in 1907.

6. That under (*k*), p. 75, *Bull.* No. 46, mark the official method "(*a*)," and insert the following:—

B. *Optional Provisional Method.*

Proceed as in (*a*) through "let stand a few minutes in the water-bath," and complete as follows:—

Filter into a beaker, add a drop or two of hydrochloric acid and 1 cc. of ammonium sulphate (75 grms. to 1 litre), digest several hours on water-bath, and filter into a tared platinum dish. Evaporate to *complete* dryness, heat to full redness, add 1 grm. of powdered ammonium carbonate, expel by heating, cool, and weigh the sulphates of sodium and potassium. Determine potassium in the usual manner.

Adopted.

6. Insecticides.

It is recommended that the methods submitted for investigation in 1905 be further studied. These methods are as follows:—

1. Work on London purple, special attention being given to the modifications proposed by Mr. Davidson for the removal of part of the colour.

Davidson's Modification.

Total Arsenious Oxide.—Place 2 grms. of London purple in a beaker, and dissolve in about 80 cc. of water and 20 cc. of concentrated hydrochloric acid at a temperature of 80°. Cool, and add sodium carbonate in slight excess, transfer to a 250 cc. flask, and bring to the mark; shake, and filter through a dry filter into a dry beaker; acidify 50 cc. with hydrochloric acid, and add sodium bicarbonate, titrating with iodine as usual.

Total Arsenic Oxide.—Acidify 50 cc. of the alkaline solution, prepared as described under "Total Arsenious Oxide," with hydrochloric acid, add 25 cc. of concentrated hydrochloric acid and 3 grms. of potassium iodide. Then proceed as directed under this determination in *Circular* 10, revised, Bureau of Chemistry, p. 4.

2. The hydrogen peroxide method for determining sulphur in sulphur dips and similar compounds, efforts being made to have all analyses made simultaneously.

3. The hydrogen peroxide method for determining formaldehyde in its modified form.

4. The methods of determining available chlorine in bleaching powder.

Motion carried.

PROBLEMS OF APPLIED CHEMISTRY.*

By Prof. GEORGE LUNGE.

It is one of the greatest honours I could covet to stand up in a room hallowed by the shades of some of the heroes of Natural Science, and to be privileged to speak on the theme I have selected. I feel that I ought to justify my claim to do so by the interest and importance of the subject. But I think it right to say at once that the title of this discourse, "Problems of Applied Chemistry," is in effect much too comprehensive, and should not be pressed home. A mere enumeration of such problems would be both tedious and useless; and how could anyone think of treating all of the more important of these problems within the space of sixty minutes? I shall have to confine myself to merely a few of those matters which might be fairly brought within the compass of the title of this lecture.

"Applied" in the narrower sense of "Industrial." Chemistry means the pressing into service of chemical principles for practical purposes, such as the extraction of valuable matters from the three realms of Nature, and the conversion of such matters (if they cannot be put to any direct use) into numerous other useful substances. The science and art of the engineer are intimately interlaced with those of the practical chemist, so that it is difficult to say which of the two has to borrow most from the other in order to carry out his objects in the most efficient manner. So much is certain—an industrial chemist cannot exist, as such, without availing himself of the resources of the constructive arts. Even the laboratory of the purely scientific chemist in these days contains numerous mechanical appliances, without which (to quote only one instance) it would have been impossible to effect the glorious discoveries made in the laboratory of the Royal Institution, in the past generally, and more particularly in quite recent times. But what could the chemical *manufacturer* nowadays do without such assistance? The practical, as distinguished from the scientific, chemist possesses, or is supposed to possess, sufficient knowledge and experience to see to the working of machines and to minor repairs without calling in an engineer, save in difficult or complicated cases, or where the work is carried out on such a scale that the services of a specialist are required, and that it pays to employ one. If a chemist lacks such knowledge, or possesses it in too limited a degree, he will have to be content to remain in the laboratory and to do the ordinary "testing," which is both a tedious and a badly-paid occupation. I am told that in this country this is far more frequently the case than either in America or on the Continent; but I must refrain from pronouncing an opinion as to how far this is due to the ordinary training of the chemists, and how far to the jealous reluctance of many unstudied managers to afford the chemist access to the real factory work, lest he acquire sufficient routine in that work to supplant themselves.

Well, granting the opportunity, how can a chemist gain experience in conducting operations on a large scale? Various ways are open for this purpose. In former times the chemical manufacturer (who only in very exceptional cases deserved to be called a real chemist) learned his trade, both on the chemical and the engineering side, as far as it was indispensable; but he learned it simply "by rote," as the saying goes. He would enter a factory as apprentice or volunteer, and there he had an opportunity of witnessing, not merely all the chemical operations, but also the building of sheds, the setting of pans and of steam boilers, the erection of the simple machinery of those days, the construction of furnaces for chemical purposes, and similar matters, and he was expected to use his hands like any ordinary workman. If he was clever and industrious, he learned in the course of years, not merely to direct the various operations at the works, but also to make improvements in details, and, perhaps, if all went

* A Discourse delivered at the Royal Institution, March 15, 1907.

well, in more important matters. To be sure, it is notorious that this never took place without large sums of money being thrown away, either in the form of misshapen or faulty apparatus and machinery, or of spoilt chemicals, and so on. And this happened to the unstudied "practical man," who, through family connections or by mere chance, had stumbled into chemical manufacturing, as well as to men who had studied the science of chemistry, and who desired to apply the knowledge thus gained to the execution of some well-known process, or to the working of some laboratory invention on a large scale. Those men who possessed a scientific foundation, were, in their turn, compelled to learn the technical side of their profession by dint of practice, just as the tailor has to learn the art of making clothes and the barber the art of shaving. A man of scientific attainments had certainly, even in the olden times, a clear advantage over the mere "practical man." He was able to make a chemical examination of his first materials, of the intermediate products, and of the finished merchandise. Sometimes, although by no means invariably, he could more easily manage to ascertain the causes of disturbances in the manufacturing processes, and to put these right again ; and often he was able to effect savings and improvements in these processes. But this advantage only held good in such cases where the chemical reactions, as such, came into play ; whilst in those cases where the mechanical side prevailed, the studied chemist, for the most part, showed less quick insight and resource than the unstudied foreman or manager, with the ultimate result that he wasted quite as much money over failures as the others did. And it is not difficult to understand that such failures happened even to eminent scientific chemists who attempted to carry out their ideas on a large scale. Their ignorance of the proper ways for translating a laboratory method into a manufacturing process was at that time remedied only in exceptional cases by the advice of an engineering expert. If such an expert was actually consulted he often did not succeed in his task, because chemical operations were outside his province, and because he tried to apply certain means, suitable to cases with which he was familiar, in cases of an entirely different nature. On the whole, the chemical manufacturer of those days felt at every turn the pinch of a mere routine experience, gathered piecemeal during the course of his daily work.

This state of affairs continued until about the middle of last century, or a little later—to be sure with marked differences in details, both in respect of local conditions and in the nature of the manufacture. To begin with the latter, we perceive that then, as indeed from the very first, several branches of chemical manufacture had their full share in the progress of mechanical engineering. To name only a few of these, we may refer to the vast field of metallurgy, to the manufacture of coal-gas, and to the extraction of sugar from beet-roots. But precisely in these cases we cannot find much proof of co-operation between the chemist and the engineer, for the former had very little to say in these industries at that time, and in most of these establishments his services were dispensed with, whilst all the resources of mechanical engineering were fully applied. The managers of such works did not come from the ranks of the chemists, but from those of the mechanical engineers; and even now that chemistry has established its proper influence upon those industries, and has produced great revolutions in them, that state of things has remained very much as before. Many other branches of manufacturing, which undoubtedly have a chemical basis, and in which to-day a large number of chemists are actually employed, were in those days carried on in a purely empirical manner, like any handicraft. I instance soap-making, tanning, brewing—indeed, all those industries which are connected with food—and above all, dyeing and tissue-printing. But towards the end of the period which we have so far had in view, we perceive the commencement of a scientific treatment of those industries. Even before then, the genius of Chevreul had thrown a flood of light on the chemical behaviour of fatty substances, and Persoz followed in the domain of dyeing fabrics. On the other hand, the more intelligent manufacturer of chemicals gradually ceased to entrust the construction of apparatus to ordinary tradesmen, and began to seek the assistance of trained engineers, so as to obtain apparatus constructed in the most rational way, and so to effect a saving in space, time, fuel, and labour. This co-operation of the various arts and sciences was distinctly promoted by the technical high schools in France and Germany, more especially the Ecole Centrale at Paris founded in 1830, and the Polytechnics at Karlsruhe, Vienna, Hanover, and Zürich, which sprang into being during the ensuing twenty-five years.

In Great Britain matters took a somewhat different course. Here the chemical industries had from the first taken their full share in the astounding development of all branches of industry which in this country has for several centuries enjoyed an uninterrupted peace, whilst continental Europe was lacerated by frequent wars, above all by the storms raging during a quarter of a century in the wake of the French Revolution of 1789. Napoleon's attempt to create industrial progress by special legislation, and by hermetically shutting off the Continent from intercourse with England, was not crowned with success ; and the industries artificially nursed by his policy mostly collapsed when, on the conclusion of peace, English merchandise was once more freely imported into France, Germany, and other countries. Thus, Great Britain had a long lead in all the fields of commerce and industry.

Some of the most important of the chemical industries have, indeed, altogether originated in this country, especially that of sulphuric acid and that of chloride of lime, both of which date back as far as the eighteenth century. But it is only fair to remember that some of the most important improvements in these manufactures are due to French inventors and French scientists. Not only that, but we must bear in mind that to France we owe the invention of the Leblanc process, which for three-quarters of a century has enjoyed a practical monopoly in the manufacture of alkali. It is curious to notice how, in this case, England has reciprocated the services rendered to her by France by the development of the other chemical industries just named. The Leblanc process, invented in 1791, and carried out on a large scale in France a few years later, could not be at once introduced into this country, owing to the fact that its first material, common salt, was burdened with an absolutely prohibitive excise duty. The abolition of this tax in 1823 acted like the wave of a magic wand, not merely in calling into life the manufacture of alkali itself, but by giving a strong impetus to all the chemical industries connected therewith, viz., those of sulphuric, hydrochloric, and nitric acid. Almost immediately the tide of inventions and improvements set in, and a few decades later we find Great Britain absolutely dominant, not merely in the branches just mentioned, but generally in the field of inorganic chemical industries. For many years, up to 1870 about, this predominance was not seriously called into question.

This splendid achievement Great Britain owes, in the first place, to the energy, business capacity, and general practical ability of her sons ; and, in the second place, to her very much greater freedom from the leading-strings of government, in comparison with Continental states ; but, thirdly, also to the special talent possessed by many Britons in the mechanical direction, to their aptitude for seizing the essence of any machinery, and to their genius for inventing new mechanical contrivances and adapting them for purposes of manufacturing and locomotion. The nation to which mankind owes the inventions of the steam-engine, of railways and steam-boats, and the displacement of manual labour by machinery in spinning and weaving, and countless other industries, such as the substitution of the Bessemer process for hand-made wrought-iron, this same nation has, up to the third quarter of last century, also manifested the greatest progress in applied chemistry.

The British manufacturer, although in those times he had frequently not studied the science of chemistry, as such, has, nevertheless, always shown special aptitude for creating, so to say, intuitively, the most suitable apparatus for operating chemical processes, the principle of which may have been discovered elsewhere.

In this manner inorganic chemical industry was developed in Great Britain up to the middle of last century to a greater extent than in any other country, by men like the Muspratts, Tennant, Gossage, Dunlop, Chance, and many others. Most of them were neither studied chemists nor engineers, but in their school any theoretically educated chemist could immensely profit for the work of factory-manager.

In close connection with this state of matters we find in England among the greatest inventors men who, at the outset, did not even possess a routine knowledge of the field in which they achieved their later successes, and who were altogether "outside the profession." Walter Weldon, the reformer of the industry of chlorine, was a journalist of high literary culture, but originally of a very slight amateur knowledge of chemistry, and not at all acquainted with practical manufacturing. Henry Bessemer was a brass-founder who, during the earlier part of his life, had nothing to do with iron. Sidney Gilchrist Thomas was a clerk in the War Department, who had never seen an iron-works when he made his epoch-making invention, and who had acquired his knowledge of chemistry and metallurgy in his spare time after office hours which most of his colleagues in England spent in the pursuit of sport, and many of his Continental colleagues in the beer-house or the wine-tavern.

(To be continued).

PROCEEDINGS OF SOCIETIES

PHYSICAL SOCIETY.

Ordinary Meeting, March 8th, 1907.

Prof. J. Perry, F.R.S., President, in the Chair.

A paper by Prof. F. T. Trouton and Mr. S. Russ on "*The Rate of Recovery of Residual Charge in Electric Condensers*" was read by Prof. Trouton.

The experiments described by the authors were undertaken in order to examine the rate of recovery of residual charge when the difference in potential of the plates is kept constant. Previous experimenters have always allowed the charge to accumulate on the plates while observing the rate of rise in potential. In that case the recovery meets with an ever increasing opposition which complicates matters. The authors have employed two methods. In the first, which was used with mica condensers, the potential, observed by an electrometer, was kept constant by means of a variable resistance which was gradually increased as the recovery current diminished. The high resistance necessary was constructed of two horizontal metal plates with ionised air between them. A movable shutter could be introduced between the plates to gradually diminish the cross section of the air resistance as required. The second method was used when the residual charge was great enough. In it the current was passed through a dead-beat galvanometer, and the value of the recovery current at each moment determined. In this case the difference of potential of the plates may be taken as constant since it was practically zero. The observations when plotted with current against time were found to lie on a hyperbola. This shows that under the circumstances of the experiments the quantity of electricity recovered up to any given time follows a law $Q = a \log (p + t)$ similar to that found by Rankine and others for the recovery of stress in overstrained elastic bodies when the strain is kept constant.

The Chairman said that together with Prof. Ayrton he had carried out a series of experiments on this subject which were described in the *Proceedings of the Royal Society* (vol. xxx.). Observations were made upon strained materials, Leyden jars, and voltameters, with the object of testing Maxwell's law. The current flowing into or from the condenser was kept constant and equal to zero, and under the conditions of the experiments the solution of Maxwell's differential equation gave for the potential v between the surfaces of the condenser the equation—

$$v = A + Be^{-\beta t} + Ce^{-\gamma t} + \ldots$$

If β was less than γ, γ less than δ, and so on, then after certain intervals of time certain of the terms became unimportant, and if the time were sufficiently large the equation for v reduced to—

$$v = A + Be^{-\beta t}.$$

He was of opinion that if the higher terms in the expression for v were maintained it would be found that the results obtained by the authors could be made to fit a formula deduced from Maxwell's theory. It was necessary to exercise caution in the selection of an empirical formula to represent the results of experiments. Two very different formulæ would often over a moderate range fit a series of results equally well.

Mr. A. Campbell said the method of using ionised air for a variable and adjustable resistance was very ingenious. A somewhat similar use of ionised air as a constant high resistance was made by Prof. McClelland (Royal Dublin Society, Feb., 1904), who found such a resistance most useful in comparing very small capacities. In the case of the celluloid and paper condenser the effects must be partly electrolytic, for moisture is present as an important factor. This might even be true in the case of a mica condenser in which the tin-foil does not make extremely good contact with the dielectric and where creeping charges might occur. Thus the effects described in the paper may not be truly dielectric.

Mr. Rollo Appleyard remarked that in the absence of details regarding the condenser it was difficult to discover how nearly or how remotely the dielectric sheets in the authors' experiments were analogous to test bars submitted to mechanical stresses in Prof. Rankine's investigations. The authors stated that their condenser was constructed of "celluloid sheets, in conjunction with layers of paper, laid on either side." This leaves in doubt the nature of the material of the conducting surfaces and the effectiveness of the contact between those surfaces and the dielectric. If it happened that the contacts were imperfect the results must be held to relate as much to what transpires at the surface as to any action within the material. Imperfect electrical contact must be regarded as analogous to mechanical slip, and the equations must be modified accordingly. Celluloid is a dielectric which, when tested between electrodes making perfect contact, exhibits practically no "electrification"; and from this it is safe to predict that it will exhibit very little residual-charge effect. After receiving the proof of the paper he (Mr. Appleyard) carried out some tests upon a sheet of celluloid 0·177 cm. thick with circular electrode surfaces 14 cm. diameter. The total pressure on the upper tin-foil electrode was 3170 grms., and the temperature 20° C. The results obtained are shown in the accompanying table.

A comparison of the above figures with the results arrived at by the authors seemed to break new ground, and a study of the differences should lead to a better understanding of these phenomena. As the authors worked with only 20 volts the attractive force between the electrodes and the dielectric would be less than in the above case. In the paper the authors had expressed their results in an arbitrary unit of time, so that it was impossible to determine whether in this respect his results agreed with those of the authors. An arbitrary unit of current had also been adopted by the authors.

Mr. W. A. Price expressed his interest in the paper,

Volts.	Galvanometer deflection after— One min.	Two mins.	Three mins. (Battery removed at two mins.).	Resistance between electrodes (megohms).
		Mercury Electrodes.		
176	118	118	− 0·5	80·5
289	232·5	232·5	− 0·5	67·0
442	348	348	− 1·0	68·5
600	464·5	464·5	− 1·0	69·7
		Tin-foil Electrodes.		
176	28	31	0·0	339
289	134	143	0·0	116
442	293	302	0·0	81
600	471	480	+ 1·0	69

and asked if the authors could give a physical explanation of the phenomena described.

Prof. Trouton said, in reply to the Chairman, that they had tried to represent their results by an exponential expression, but the result was not nearly so good as that obtained from the formula given in the paper. Of course with more constants an exponential expression could be used. He had found that their formula fitted the results of the Chairman and Prof. Ayrton. In reply to Mr. Campbell and Mr. Appleyard he said that possibly there might be electrolytic action, but most of the phenomena described were due to residual-charge effects. With reference to the units, he said the times were expressed in seconds, but the unit of current was arbitrary.

The remaining papers on the agenda were postponed.

NOTICES OF BOOKS.

The Toxins and Venoms and their Antibodies. By Em. Pozzi-Escot. Authorised Translation by Alfred I. Cohn, Phar.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1906.

This book contains an account in outline of the action of toxins and venoms considered mainly from a physiological point of view. The substances which the author treats include, not only the true toxins, but also various nitrogenised alkaloidal bases which have strong toxic properties and appear to be the products of the decomposition of true toxins. The latter are sub-divided into—(1) Vegetable and Animal Toxins, (2) Microbial Toxins, and (3) Venoms, and in each class the characteristic properties and symptomology are shortly described, and the question of immunity is also considered; the chemical nature of toxins and allied substances, however, is passed over, and the whole treatment is very slight. The little book may perhaps be useful as a short *résumé* of the very important work which has recently been done on the toxins, but there are omissions and misprints which call for rectification in a later edition. Thus, no account of cantharidine is to be found, though the poisons of wasps, bees, scorpions, &c., are noticed, and the poison of the mussel, mytilotoxin, is misnamed methylotoxin on the last page.

Inorganic Qualitative Chemical Analysis. By William Stowell Leavenworth, M.Sc. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1906.

The output of text-books of qualitative anyalsis has reached a very high level in recent years, and the appearance of every new book on the subject awakens in the mind the doubt whether there is room for yet another. The examination of this book enables us to give a favourable answer as to its right of existence, although not without reservations, in view of the similarity in scope and style between it and many other practical text-books. It occupies an intermediate position between a skeleton outline of the subject and a lengthy detailed treatise, and the author has done a very useful work in endeavouring to develop the student's independence of thought and initiative. It is made impossible for him to do his work mechanically, and at every turn he is forced to think and reason for himself. Thus, he devises his own scheme of analysis which is fixed in the memory by means of clear outlines of the groups. Organic salts are used as the group reagents for the detection and separation of inorganic acids, and thus the use of inorganic acid salts in the separation of the groups is altogether avoided. The appendix gives full data concerning the strengths of solutions used, and also contains a discussion of the reactions of some rare metals, and on the whole the book is at least not inferior in value to some of the best of its kind.

Food for Plants. By Harris and Myers. New Edition, with Supplementary Notes. New York: William S. Myers, F.C.S.

The authors of this book succeed in making out a strong case in favour of the use of nitrate of soda as a fertiliser. The most satisfactory methods of applying it are emphasised, and various rules are given which the farmer is advised to follow carefully; moreover, the Bulletins of different Agricultural Experimental Stations are quoted to show the results of the many experiments which have been made in the use of this fertiliser. Most of the information and hints would appeal to the American farmer rather than to the English agriculturist, who has recognised the value of nitrate of soda, and uses it freely. The illustrations are very telling, and the applications of nitrate to all classes of crops are considered, while numerous results of the analysis of all kinds of manures are tabulated.

CORRESPONDENCE.

BIOTIC FORCE.

To the Editor of the Chemical News.

Sir,—In considering the possibility or otherwise of vital force, recently called biotic force, expressing a special form of energy, we should keep in view the fact that biochemical changes in their essential take place at infinitely small distances among highly complex molecular structures, and that physico chemical processes may gradate in a manner not at all attainable in the inorganic world.

Biotic force, if such exist, should, we might think, present some relationship to nervous force, as expressing a transference of energy, and the latter force has before now been associated in its manifestations with those of electrical energy.

As regards the mechanism of metabolic changes a graphic picture is given by Macalister as follows:—

"All protoplasm is capable of being stimulated to metabolism and the discharge of energy by external agencies, but in the differentiation that characterises the development of animals, a physiological division of labour takes place in many cells, whereby the contractibility of one part of the apparatus becomes intensified, constituting molecular tissue, while the capacity of receiving sensations becomes concentrated in other cells of the surface-layer."

It might be suggested that a mere question of relatives as applied to the space in which bio-chemical changes take place is sufficient to account for vital phenomena as resulting from the application of the already admitted forms of energy, and the difference in the manifestation of these forms of energy from those taking place in the inorganic world.

At the same times, caloric energy is, perhaps, of the known forms, the most usual concomitant with vital manifestation, is always associated with the transformation of chemical energy into mechanical and physiological work, and can itself induce chemical action.

Hence, from the known forms of energy we may say that these themselves may account for all the changes taking place in physiological action and ask if the present experimental evidence and scientific deduction is sufficient to warrant the establishment of a new form of energy, the manifestations of which are due to biotic force.—I am, &c.,

J. C. THOMLINSON.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 10, March 11, 1907.

Direct Dehydration of Dimethylisopropylcarbinol, $(H_3C)_2C(OH)-CH(CH_3)_2$.—Louis Henry.—The direct dehydration of dimethylisopropylcarbinol produces tetramethylethylene. The process was carried out by first obtaining the tertiary alcohol by the action of magnesium methyl bromide upon ethyl isobutyrate and then dehydrating with acetic anhydride. On distillation, a liquid boiling at 56—58° was obtained, and another boiling at 72—73°, being three-quarters of the whole product. Thus the operation acts in two ways:—(*a*) Methylisopropylethylene, $H_2C=C(CH_3)-CH(CH_3)_2$, is formed, boiling at the lower temperature; (*b*) tetramethylethylene, $H_3C>C=C<CH_3$ / H_3C / CH_3, is the main product, boiling at 72—73°.

An Accurate Method of Separation of Ammonia and Monomethylamine.—Maurice François.—Every method of preparation of monomethylamine furnishes it mixed with a considerable quantity of ammonia, which has to be eliminated. The author has found the use of yellow oxide of mercury most successful for the purpose, since it combines with ammonia to form ammonio-mercuric oxide, and leaves the monomethylamine untouched. It is equally applicable to other very volatile and gaseous amines, furnishing products absolutely free from ammonia. In the case of dissolved amines the product contains less than 2 1000 of ammonia. Both a dry and a wet method of purification of amines by mercuric oxide are described.

Constitution of Nitrogen Derivatives of Ethylbenzoylacetate.—A. Wahl.—The author describes certain compounds formed by the reaction between ethylbenzoylglyoxylate and phenylhydrazine under varying experimental conditions and with different relative proportions of the two components. Mixed in equimolecular quantities, an additional product, $C_{17}H_{18}N_2O_3$, is obtained, and, losing H_2O, becomes a monophenylhydrazone of ethylbenzoylglyoxylate, $C_{17}H_{16}N_2O_2$, a yellow crystalline body. It is found to be identical with ethylbenzeneazobenzoylacetate, and from this fact is deduced the constitution—

$$C_6H_5-CO-C(=N-NH-C_6H_5)-COOC_2H_5$$

The β-Chlorethyl and Vinyl Ketones. Fixation of the Sodium Derivatives.—E. E. Blaise and M. Maire.—It has been previously pointed out that the double bond of the vinyl ketones has very marked addition properties. It causes direct fixation of both primary and secondary amines and the various organic sodium derivatives. The sodium derivatives have always an alkaline reaction, and the vinyl ketones respond readily to the action of alkalis; hence one part of the non-saturated ketone is always polymerised, and from regard to the yield it pays better to react with the sodium derivatives not upnn the vinyl ketones, but upon the corresponding β-chlorethyl ketones. The author describes the following operations:—1. Sodium acetyl-acetic ether reacting with β-chlorethylethyl-ketone produced ethyl-octanedione 2.6-methyloate, which was converted into the ring compound, 3-ethyl-Δ2-cyclohexanone 6-methyloate of ethyl:—

$$CH_3-CO-CH(CH_2-CH_2-CO-C_2H_5)-CO_2C_2H_5 \rightarrow CH_3-CO-C(CH_2-CH_2-C_2H_5)=CH-CO_2C_2H_5 \rightarrow CH_3-CO-C(CH_2-CH_2-C_2H_5)=CH-CO-CH$$

2. Sodium acetyl-acetone reacting with β-chlorethyl-ethyl-ketone gave ethylone-3-octanedione-2.6, which yielded the ring compound 3-ethyl-6-ethylone-Δ2-cyclohexanone:—

$$CH_3-CO-CH(CH_2-CH_2-CO-C_2H_5)-CO-CH_3 \rightarrow CH_3-CO-C(CH_2-CH_2-C_2H_5)=CH-CO-CH$$

3. Ethyl-sodium malonate reacting with β-chlor ethyl-ethyl-ketone produced heptanone-5-oate of ethyl-1-methyl oate of ethyl-2, and the corresponding dibasic acid, decomposing when heated to give γ propionyl-butyric acid:—

$$C_2H_5-CO-CH_2-CH(CO_2C_2H_5)_2 \rightarrow C_2H_5-CO-CH_2-CH_2-CH_2-CO_2H \rightarrow CH_2(CO-CH_3)-CH_2-CH_2-CO_2H$$

This reaction would afford an excellent method of preparation of δ-ketonic acids if δ-chloro-propionyl chloride were more readily obtainable.

MISCELLANEOUS.

Society of Public Analysts.—The Council of the Society of Public Analysts has recently appointed Mr. Julian L. Baker Editor in place of the late Dr. Sykes.

The French Government has just conferred the Cross of the Legion of Honour on Professor P. A. Guye, Director of the Laboratories of Technical and Theoretical Chemistry in the University of Geneva.

Business Announcement.—The old-established firm of H. K. Lewis has just completed an important extension of their premises at 136, Gower Street, by the inclusion of 24, Gower Place, adjoining. The two shops have been made into one, the older portion being utilised chiefly as the Secondhand Department, where surplus books from the Library and other secondhand stock may be inspected. The new shop faces Gower Street and Gower Place, and affords greater convenience to customers for inspecting the latest books in all branches of Medicine, Surgery, and general Science. The Library is entered from the end of the shop, and has three windows facing Gower Place. Subscribers are able to examine the books on the shelves when making exchanges, and convenience for writing or making extracts is provided, the idea being to make this department a reading room for subscribers, especially those residing in the suburbs or the provinces. The telephone in this room is free for subscribers' use. Lavatory accommodation is also provided. The premises, which will still be known as 136, Gower Street, are within a minute's walk of the Metropolitan Station, and the new Tube Station at the junction of Tottenham Court Road, Euston Road, and Hampstead Road is only a few minutes' distance. The termini of the Great Western, Great Central, London and North Western, Midland, Great Northern, and Great Eastern are thus within easy access, while the new north and south tubes and the numerous lines of omnibuses bring the south-western and southern districts within comfortable reach.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2471.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 149).

Confirmatory Experiments and References (continued).

Solubility of Metastannic, Antimonic, and Silicic Acids in Ammonium Sulphide.—200 mgrms. metallic antimony and 300 mgrms. metallic tin were treated in separate experiments by P. 3 and the procedure described in Note 4 : clear solutions were obtained on adding the acid solution to the alkaline ammonium sulphide solution.

The following experiments show that the residue from P. 3 may be treated directly with ammonium sulphide, but that this process is ordinarily a longer one than that described in the Note.

200 mgrms. Sn as dehydrated metastannic acid, previously heated at 120°, were warmed gently with successive 10 cc. portions of the ammonium polysulphide reagent in a covered casserole for five to ten minutes, with frequent stirring ; in the first treatment considerably more than half of the tin dissolved ; after the second treatment only about 20 mgrms. were left undissolved, and two more treatments dissolved this completely. The experiment was repeated, using colourless ammonium monosulphide in place of the yellow polysulphide, the same results were obtained.

500 mgrms. Sn as dehydrated metastannic acid were treated with successive 10 cc. portions of yellow ammonium sulphide in a pressure bottle at 70—80° ; practically all dissolved in two ten-minute treatments.

200 mgrms. Sn as dehydrated metastannic acid dissolved in 10 cc. ammonium monosulphide in a pressure bottle at 80° in about ten minutes, and another portion of about 100 mgrms. Sn dissolved in the same solution on further heating.

200 mgrms. Sb as hydrated Sb_2O_5 previously heated at 120°, were treated in a covered casserole with ammonium polysulphide ; it dissolved only very slowly, and several treatments were necessary to effect complete solution. As with metastannic acid, the use of the pressure bottle hastened the solution, but antimonic acid dissolved even less readily than metastannic acid.

100 mgrms. dehydrated silicic acid were warmed for fifteen minutes with 20 cc. ammonium monosulphide ; the filtrate was acidified, evaporated to dryness, and tested for silica by P. 5 ; very little, if any, gas evolution was obtained, thus showing that SiO_2 is insoluble in ammonium sulphide. In another experiment only a few mgrms. (1 to 3) SiO_2 dissolved in 30 cc. boiling ammonia (0·96) in fifteen minutes.

P. 5, N. 2 : *The Test for* SiO_2 *with* HF *and* H_2SO_4.—One and 2 m.grms. of dehydrated H_2SiO_3 were treated as described in the first paragraph of P. 5 ; evolution of gas took place at room temperature, and was easily seen in both cases.

One and 2 mgrms. SiO_2 as felspar, which had been well purified from free silica by long-continued boiling with Na_2CO_3 solution were treated in separate experiments according to P. 5 ; there was no evolution of gas in the cold, but a distinct one took place on warming.

500 m.grms. $BaSO_4$, 100 mgrms. TiO_2, 100 mgrms. tantalic acid, and 150 mgrms. niobic acid were treated by P. 5 ; no evolution of gas was observed in the cold nor on warming, provided the solid had been previously heated with the strong H_2SO_4 to remove air bubbles.

A filter (Schleicher and Schüll, No. 597) 11 cm. in diameter, with an ash stated to be 0·0028 grm., was treated by P. 2, to destroy organic matter, and the residue by P. 5, to test for silica ; bubbles of gas were clearly seen.

In a series of experiments an attempt was made to test for silica by adding HF to the dry solid, and allowing the SiF_4 evolved to act on a drop of water held in the loop of a platinum-wire near the solid. The best conditions were found to be to add less HF than corresponded to the silica present, to allow the reaction to continue until almost all the HF was destroyed, the action being accelerated by stirring with a heavy platinum-wire, and then to warm the mixture gently, while holding the drop of water near the solid. Even under these conditions, however, the drop did not become turbid when less than 5 mgrms. SiO_2 were used, although an evolution of gas doubtless took place, as was shown by a hissing sound.

P. 5, N. 3 : *Action of Hot* H_2SO_4 *on Platinum.*—Five cc. H_2SO_4 (1·84) were evaporated to 2 cc. in an open platinum crucible within two or three minutes, cooled, diluted with 5 to 10 cc. water, and H_2S passed into the hot solution for some minutes ; a brown coloration appeared quickly, but no precipitate settled out.

Five cc. H_2SO_4 (1·84) were boiled for fifteen minutes in a covered platinum dish previously weighed, cooled, diluted, and saturated hot with H_2S ; a precipitate of PtS_2 estimated to contain 2 to 3 mgrms. Pt was obtained, and the dish had lost 3 mgrms. in weight.

P. 5, N. 4 : *Action of* H_2SO_4 *and* HF *on Minerals and other Substances.*—Each of the following substances was treated with the stated result by the following procedure, which is similar to the regular process, P. 4—6, except that in these experiments the substance was digested for a longer time with hot concentrated H_2SO_4. One grm. was digested for several minutes in a covered platinum dish with 10 cc. HNO_3 (1·42). Three cc. H_2SO_4 (1·84) were then added, the mixture was evaporated to distinct fuming, and maintained at that point for ten minutes. Five cc. HF were added, the mixture was digested for fifteen minutes on a water-bath, and then evaporated until thick acid fumes were given off ; 3 cc. HF were added, and the mixture was again evaporated to fuming. Thirty cc. water were added, the mixture was boiled for fifteen minutes, cooled, diluted to 100 cc., and the residue washed once by decantation. Thirty cc. saturated Na_2CO_3 solution were then poured over the residue, and the mixture was allowed to stand, with frequent stirring, for fifteen minutes. The solution was decanted, and the residue washed twice with water, after which it was treated with 30 cc. HCl (1·02). A large residue was left after the final treatment with HCl by cassiterite SnO_2, emery Al_2O_3, chromite $FeO.Cr_2O_3$, rutile TiO_2, cinnabar HgS, molybdenite MoS_2, tourmaline, beryl $Be_3Al_2Si_6O_{18}$, and columbite $Fe(Nb,Ta)_2O_6$. About a third of the molybdenite was decomposed by the HNO_3 with separation of some molybdic acid, which dissolved in the H_2SO_4. Cinnabar, rutile, and beryl were much attacked by H_2SO_4, and columbite by HF, but the other substances were attacked not at all, or only very slightly, by any of the reagents :—Fluor-spar CaF_2, chrome yellow $PbCrO_4$, wulfenite $PbMoO_4$, and vanadinite $3Pb_3V_2O_8.PbCl_2$, were attacked by HNO_3 and by H_2SO_4 ; titanite $CaTiSiO_5$, garnet $(Ca,Mg,Mn,Fe)_3Al_2Si_3O_{12}$, a cement, and some slags containing lead or calcium, were attacked by these acids, and also by HF. All left, after the treatment with HF and H_2SO_4, a white residue, which, after the treatment with Na_2CO_3, dissolved completely in HCl. The white residue therefore contained only insoluble sulphates, such as $PbSO_4$,$CaSO_4$; and the substances were completely decomposed by the treatment with HNO_3, H_2SO_4, and HF :—Wolframite $(Fe,Mn)WO_4$, menaccanite $FeTiO_3.Fe_2O_3$, and Prussian blue were decomposed by H_2SO_4, and all left a residue insoluble in dilute H_2SO_4, which dissolved completely, or nearly so, in Na_2CO_3 :—Magnetite Fe_3O_4, cryolite Na_3AlF_6, basalt, granite, monazite, a uranium ore, and a number of slags were

* From the *Technology Quarterly*, xix., No. 3 September, 1906.

completely decomposed after the treatment with HNO_3, H_2SO_4, and HF, and dissolved completely in the dilute H_2SO_4.

For the action of HF and HNO_3 on some other difficultly soluble native silicates, see *Technology Quarterly*, 1903, xvi., p. 126; also CHEMICAL NEWS, xciii., p. 173.

P. 5, N. 4 and 5: *Solubility of Sulphates in Concentrated and Dilute* H_2SO_4.—100 mgrms. and 150 mgrms. Ba as $BaSO_4$ were strongly heated with 2 cc. concentrated H_2SO_4; a clear solution resulted in the first case, but not in the second. $BaSO_4$ was precipitated at once when a little water was added.

For the solution of $PbSO_4$ in concentrated H_2SO_4, see C. E. on P. 26, N. 1.

Ten, 15, and 20 mgrms. Ca as $Ca(NO_3)_2$ were added in separate experiments to 20 cc. H_2SO_4 (1·20); with the 20 mgrms. a precipitate separated at once, and with the 15 mgrms. after about five minutes, while with the 10 mgrms. none formed, even after several hours.

300 mgrms. Al, 300 mgrms. Fe, 100 mgrms. mercuric Hg, and 150 mgrms. Cu, all as sulphates, were in separate experiments boiled with concentrated H_2SO_4, cooled, diluted, and again boiled as described in the Procedure; the anhydrous $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ dissolved completely after about three minutes' boiling; the anhydrous $CuSO_4$ and the $HgSO_4$ dissolved at once on warming.

To 100 mgrms. Cr as $Cr_2(SO_4)_3$ in solution as green sulphate 2 cc. H_2SO_4 (1·84), were added, and the solution was evaporated until thick acid fumes came off; the mixture was cooled, diluted, and boiled, the whole treatment being as in the Procedure; the resulting solution was green, and from its colour was estimated to contain 10 to 15 mgrms. Cr; the remainder of the chromium was left as a very finely divided light pink powder, anhydrous $Cr_2(SO_4)_3$:—This experiment was repeated, except that the H_2SO_4 was heated only until slight fumes appeared; no pink precipitate separated, and on boiling with water a clear green solution was obtained.

100 and 200 mgrms. Cr as precipitated $Cr(OH)_3$ were dissolved in 5 cc. H_2SO_4 (1·84) and 20 cc. water; the solutions were evaporated to about 2 cc., cooled, diluted, again boiled, and filtered; a very finely divided grey to pink powder, anhydrous $Cr_2(SO_4)_3$, was obtained, which ran through the filter. The precipitate was allowed to settle, and the solution was decanted and boiled with NH_4OH; it was colourless, and gave scarcely any precipitate of $Cr(OH)_3$. The anhydrous sulphate was boiled for fifteen minutes with dilute H_2SO_4; only a few mgrms. dissolved. The sulphate was found to be slowly dissolved by a concentrated Na_2O_2 solution owing to oxidation to chromate.

500 mgrms. Sb as $SbCl_3$, 50 mgrms. antimonic Sb ($SbCl_3$ previously boiled with HNO_3 and HCl), and 500 mgrms. Bi as $Bi(OH)_3$ were heated in separate experiments with 3 to 5 cc. H_2SO_4 (1·84), evaporated to 2 cc., diluted to about 20 cc., and again boiled. With the antimonous salt a crystalline precipitate was obtained on evaporating the H_2SO_4 solution; this precipitate dissolved when the 20 cc. water were added, but an amorphous precipitate formed when much more water was added. The antimonic antimony was precipitated in the concentrated H_2SO_4 as an amorphous powder, and more of this precipitate separated on dilution; the dilute H_2SO_4 solution was filtered, and the amount of antimony contained in the filtrate was estimated by precipitating with H_2S to be about 10 mgrms.; the residue insoluble in H_2SO_4 was washed with water, and dissolved in boiling HCl, and to the solution $BaCl_2$ was added; only a slight precipitate of $BaSO_4$ was formed, showing that the residue was an oxide or hydroxide, not a sulphate. In the experiment with bismuth the hydroxide dissolved in H_2SO_4, and a crystalline precipitate (sulphate) separated from the hot concentrated H_2SO_4, but the larger part of this dissolved on adding the water, provided the solution was kept cold; a precipitate (of oxysulphate) appeared when this solution was heated; the filtrate from this was treated with NH_4OH, and a precipitate was obtained which was estimated to contain 20 to 50 mgrms. Bi.

P. 5, N. 6: *Decomposition of Silver Salts by* H_2SO_4.—500 mgrms. Ag as precipitated AgCl, 500 mgrms. Ag as fused AgCl, 100 mgrms. Ag as precipitated AgCN, and 100 mgrms. Ag as precipitated AgI were treated with H_2SO_4 as described in P. 5; there was a residue in each case. HCl was added to the H_2SO_4 solution; a small precipitate of AgCl was then obtained, showing that some of the silver salt had been decomposed. The residues were boiled with 5 cc. H_2SO_4 (1·84) in a covered casserole for several minutes; AgI and AgCN dissolved readily in less than five minutes, and almost all the AgCl in less than ten minutes.

500 mgrms. Ag as AgCl were boiled with Na_2CO_3 solution (as described in P. 6) for fifteen minutes; the AgCl precipitate quickly turned black. The Na_2CO_3 solution was acidified with HNO_3, and $AgNO_3$ added; a precipitate of AgCl, estimated to contain 2 mgrms. Ag, formed, showing that only this amount of Ag as AgCl had been converted into silver oxide.

(To be continued).

DAIRY PRODUCTS, FOODS AND FEEDING-STUFFS, SUGAR, TANNIN, AND MEDICINAL PLANTS AND DRUGS.*

REPORT OF COMMITTEE B.—(E. B. HOLLAND, *Chairman*).

1. MEDICINAL PLANTS AND DRUGS.

IT is recommended—

1. That the present provisional method for the assay of opium products be made official. (Proceedings, 1905, *Bull.* 99, p. 162; *U. S. Pharmacopœia*, Eighth Revision, p. 329, with additions).

Referred to the Referee for 1907 for recommendation and final action by the Association.

2. That the present line of work be continued by the Referee on medicinal plants and drugs.

Adopted.

2. FOODS AND FEEDING-STUFFS.

It is recommended—

1. That the König and modified König method for crude fibre be dropped. (See Proceedings, 1903, *Bull.* No. 81, p. 38).

Adopted.

2. That the slightly modified Ellett-Tollens method for methyl-pentosans be tested again next year by the Association. (*Z. Landw.*, 1905, liii., [1], 13).

Adopted.

3. Upon motion by Mr. Peter, the Association voted to instruct the Referee for 1907 to study the temperature and time of drying of ether extracts.

Passed.

3. DAIRY PRODUCTS.

It is recommended—

1. That the method of double extraction be adopted as provisional for the determination of fat in condensed milk, the directions to be given as follows:—

Fat.—Extract the solid residue of about 5 grms. of a 40 per cent solution with ether in the usual manner; dry, leave tubes in a dish containing 500 cc. of water or more, for two or three hours; dry, extract again for about five hours, and determine fat as under Milk. (*Bull.* 46, p. 54).

Adopted.

2. That the Gottlieb method (*Landw. Versuchs. Stat.*, 1892, xl., 1) be made provisional for the determination of fat in milk.

Referred to Referee for 1907 for further recommendation.

* Extracts from the Proceedings of the American Association of Official Agricultural Chemists, 1906.

3. That the conversion factor for protein in milk and dairy products be changed to 6·38 throughout the methods.

Referred to committee on unification of terms for reporting analytical results.

4. That the study of methods of analysis of condensed milk be continued with special reference to the determination of lactose and sucrose in the sweetened product.

Adopted.

4. Sugar.

Recommendations Pending from 1905.

The following recommendations are made in regard to questions referred from 1905 for action. (See Proceedings, 1905, *Bull.* 99, pp. 18—25, p. 155; *Circular* 26, p. 5):—

Chemical Methods.

1. That the methods selected by the International Committee for unifying sugar analysis, now provisional, be made official with the exception of paragraph 7, which should be eliminated, and paragraph 8, upon which action should be deferred. (See Proceedings, 1902, *Bull.* No. 73 Bureau of Chemistry, p. 58).

Adopted.

2. That action upon recommendations 3 and 4 be deferred until 1907. These recommendations are as follows:—

3. That method (*a*) for the determination of copper in the cuprous oxide precipitate, requiring reduction in hydrogen (see *Bull.* No. 46, p. 37) be dropped as an official method of this Association.

4. That methods (*c*) and (*d*) for the determination of copper in the cuprous oxide precipitate, requiring the electric deposition of the metal (see *Bull.* No. 46, p. 38), be dropped as official methods of the Association.

Action deferred as recommended.

3. That action for the adoption of Low's thiosulphate method for determining copper in the cuprous oxide be deferred until the original method and its modification be compared by the Association.

Adopted.

Molasses Methods.

Of the five recommendations deferred from 1905 for action, No. 1 is covered by recommendation No. 3 under general recommendations on sugar, 1906, which follows, while action on Nos. 2, 3, 4, and 5 is deferred until further co-operation is obtained from interested chemists. (See *Circular* 26, p. 5, or *Bull.* No. 99, p. 24.

General Recommendations, 1906.

It is recommended—

1. That further work be done upon the comparison of moisture methods for molasses and massecuites before action be taken by the Association.

Adopted.

2. That when increased accuracy is desired in the determination of reducing sugars in commercial products on account of the danger of contamination in the precipitated cuprous oxide, only such methods be followed as provide for a direct determination (electrolytic or volumetric) of the reduced copper.

Adopted.

3. That in the optical methods for the analysis of dark coloured massecuites, molasses, and other low grade products, the normal weight of substance may be made to some multiple of 100 cc., according to the extent necessary for accurate polarisation. This normal weight may be weighed out directly and made up to the desired volume, or taken from a solution prepared by dissolving a larger amount of the material (50 to 100 grms.) with water to a definite weight or volume. The latter method is to be preferred with non-homogeneous materials, such as massecuite, to secure greater uniformity of sample.

Adopted.

4. That in the estimation of sucrose by the gravimetric method the calculation by the factor 0·95 (*Bull.* 46, p. 39, bottom line) be made only upon the reducing sugars estimated as invert sugar. In making this calculation reducing sugars previously present, which require to be subtracted, must also be expressed as invert sugar.

Adopted.

5. Provisional: That reducing sugars in mixtures either before or after inversion may also be expressed as dextrose, in which case the calculation of the true percentages of sucrose and other sugars may be made by appropriate conversion factors and formulæ. (Browne, "Analysis of Sugar Mixtures," *Journ. Am. Chem. Soc.*, April, 1906).

6. Provisional: That for the estimation of dextrose, invert sugar, maltose, and lactose, under uniform conditions of analysis, the method and table of Munson and Walker be adopted provisionally by the Association. (Munson and Walker, "Unification of Method for Reducing Sugars," *Journ. Am. Chem. Soc.*, June, 1906).

Upon the suggestion of the Referee action on recommendations 5 and 6 was deferred, since but little co-operative work had been done.

7. That the questions of the influence of the lead precipitate, and the use of hypochlorites, hydrosulphites, and other agents for decolorising in optical analysis, and the use of clarifying agents before estimating reducing sugars, be investigated further before decisive action is taken by the Association,

Adopted.

8. That the co-operation of sugar chemists not members of the Association be invited, to secure a greater expression of opinion upon matters pertaining to improvement of analytical methods.

Adopted.

5. Tannin.

1. The report of the Referee on tannin was not received until after the report of Committee B had been made, but it was considered by the committee and a supplemental report made by Mr. Kebler in regard to the recommendation of the Referee that "the tannin section of the Association of Official Agricultural Chemists abandon the appointment of referee and associate referee and omit supervision of the tannin method." The committee recommended that the tannin work of the Association be continued, and the recommendation was adopted by the Association.

2. Upon motion by Mr. Veitch, the method on tannin submitted by the Referee in 1905 (*Bull.* No. 99, p. 123), as revised by the committee on revision of methods, 1906, was adopted as a provisional method, the changes made by the committee being almost exclusively in manner of statement, &c.

PROBLEMS OF APPLIED CHEMISTRY.*

By Prof. GEORGE LUNGE.

(Continued from p. 153)

Peculiar to England is also the following case, very different from those just quoted, but also illustrative of the ways of British inventors. William Henry Perkin, whose jubilee was celebrated last year amid the concourse of all civilised nations, had, at the early age of sixteen, entered Hofmann's laboratory in London. Already, two years afterwards, whilst working at the synthesis of quinine (a task not accomplished up to date), he discovered the colouring matter called "mauve," the forerunner of all colours produced from coal-tar: and only a year later, at an age when, on the Continent, the great majority of young men are either still at school, or at least entirely innocent of any taste for practical life, and when they only enter upon their theoretical studies, he built a factory for producing his mauve, which at once proved a success and

* A Discourse delivered at the Royal Institution, March 15, 1907.

laid the foundation for his splendid work in after life. This is not the place to enlarge upon his later career, which is almost unique in combining inventive genius with the true spirit of pure science.

We need not be surprised to find that sometimes even the most eminent practical men threw away much time and capital on inventions which, in the end, turned out failures. Sometimes this was due to the fact that, owing to their ignorance of the scientific principles of the case, they hit upon a wrong idea and pertinaciously clung to it, unmoved by constant mishaps which they hoped to overcome by patience and perseverance. But not unfrequently failures occurred, even where the original idea was a good one, which, in the end, was carried to a successful issue. The cause of this may be that the inventor had overlooked some difficulty, apparently unessential, but in effect fatal to success. Or else the proper mechanical means for carrying out the idea were not discovered by the inventor nor the experts consulted by him. I beg leave to illustrate this by a remarkable instance. One of the great problems presented to applied chemistry in the last century, at which many inventors in all industrial countries have been working, was the utilisation of "alkali-waste," that is the residue resulting from the extraction of crude soda by the Leblanc alkali process, which occupies a large space, and which for generations caused an unbearable nuisance for miles around the works by contaminating air and water. The first partial success in this direction was scored in 1861 by Ludwig Mond at Cassel—later on at Widnes, and by Max Schaffner at Aussig. But the endeavours to solve that problem are much older. One of the first patents referring to it was taken out in 1837 by Gossage, one of those great captains of English chemical history whose name I have already cited. Already, at that date, he had conceived the idea of decomposing and utilising the calcium sulphide, which is the principal constituent of alkali-waste, and which, at the same time, is the cause of the nuisance produced by that waste. The idea was to treat the waste with moist carbonic acid, which interacts with the calcium sulphide to form calcium carbonate and hydrogen sulphide. Gossage quite rightly recognised a number of the conditions necessary for realising that reaction, but unfortunately not all of them. To mention only one thing in which he failed: neither Gossage himself, nor anybody else for many years afterwards, hit upon a practicable method of dealing with the dilute hydrogen sulphide formed. After working incessantly at this problem for seventeen years, Gossage believed success within his grasp. Most unfortunately, he was not merely mistaken, but committed a serious financial miscalculation as well. In his over-confidence he launched out into a big speculation by contracting with all alkali manufacturers of Widnes (then the greatest centre of that industry in the whole world) for the treatment of their waste during a number of years. But it soon became manifest that there were unforeseen difficulties not yet overcome. The expense of the treatment, moreover, exceeded the value of the products. Still, Gossage's good faith was recognised on all sides, and all the alkali makers but one released him from his ruinous contract. That single exception, however, proved sufficient to cripple the inventor financially, though his name was even then one of the most honoured in his profession, not merely in England, but also abroad, and though it was common knowledge that he had spent the best years of his life on that thankless task. As late as 1861 he firmly proclaimed his conviction that he was right after all, in a discourse delivered before the British Association. Well, he *was* right, but the missing links in the process were only discovered in 1883 and 1887, and led to the application of that process at all the Leblanc works. This final success is connected with the names of Carl Friedrich Claus and of Alexander Chance.

Just about the time of which I have been speaking, I tried, after absolving my University studies in my native country, Germany, to make my way there in the chemical industry, which, at that time, was certainly in a very backward state. Accordingly, in 1864, I resolved to try my luck in this country, which occupied the first place in this respect as well as in many others. One of my first steps, after arriving in England, was to call at the Royal Institution with a letter from my teacher, the immortal Robert Bunsen, introducing me to the Professor of Chemistry, Edward Frankland, who received me with the utmost kindness, and whose powerful word greatly smoothed my progress. In coming to England for my practical education, I followed the example of many German chemists, of whom I will only quote a few of the most eminent names—Caro, Pauli, Martius, Peter Griess, and Ludwig Mond. The two last-named have permanently associated themselves with this country; whilst the three first-named, as well as many other German chemists who had found a temporary home in England, returned later on to their own country; and these very men have been in the forefront of those to whom is due the remarkable development of German chemical industry, which took place almost at the same time as its political rise, a coincidence which is probably not at all accidental. I myself remained twelve years in England, and only left when called to my professorial chair in Switzerland.

The reason for the sudden and intense blossoming out of the chemical industry in Germany, after being long dormant, and for its firm and healthy rooting in a soil long prepared by the general spread of scientific education, is perfectly clear. Up to that time the German professor, as well as his students, had been frequently held up to ridicule, not merely abroad but at home as well, as idealistic dreamers, unsuited to the wants of real life and to the requirements of trade and manufacture, and in this there was only too much truth, so long as they were not in intimate touch with men of practice. But at last an amalgamation between these two classes of men took place, and was greatly furthered by the World's Exhibitions, chiefly that held in London in 1862, and, moreover, by the very lessons learned by the German students during their stay in England. Without laying aside their scientific armour, they profited by what they had seen of the co-operation of chemistry and engineering, and, generally speaking, of the interaction of science and practical life. Within a very few years there arose those enormous establishments at Ludwigshafen, Hochst, Elberfeld, Berlin, Darmstadt, and elsewhere, which are conducted on a scientific basis, but with the most extensive utilisation of all the attainments of manufacturing experience. Several of these have now a staff of a couple of hundred chemists and of dozens of fully-trained engineers. But although at present Germany certainly holds the foremost position in many branches of chemical industry, it would be unfair to award to her the only palm for progress in this branch of human work. Austria, France, Switzerland, and Belgium have all made immense strides in that direction; of America we shall speak anon. And what of Great Britain? Well, she has certainly not stood still, and she is still one of the greatest homes of industrial chemistry, but one cannot blind oneself to the fact that her progress in this line has not been quite so rapid as that of the other countries just named, to say nothing of the United States, whose chemical industry was hardly in existence at the beginning of that new epoch, but which now is second to none but England and Germany. To some extent the comparative slowness of development in this country is not absolute, but merely relative. It is clear that those who are already well ahead cannot, within a given time, cover as much ground as those who start late, since there is so much less leeway to make up; hence the quicker progress made by the late starters does not mean any real superiority, provided always that the former class are not actually outstripped in the race. The question whether this has really come to pass in this or in that field of chemical industry in the struggle for life between the English chemical manufacturers and their Continental and American rivals, is too wide and too

delicate a topic to be touched upon now. But so much you will allow me to say—if we confine ourselves to a comparison of English and German chemical industries, I have surely laid sufficient emphasis upon the fact that the Germans have immensely profited from the English in the matter of practical manipulation and in the co-operation between chemists and engineers. Why should not the English then turn the tables on the Germans, and profit, in their turn, by giving a wider scope to the scientific treatment of industrial problems in their factories than has hitherto been the rule? Seeing that in pure science the people of Great Britain have never lagged behind *any* other nation, and that, on the contrary, the land of Newton and Faraday has been a beacon to all others at more than one epoch, there is absolutely no valid reason why she should now, or at any other time, be behind any other in the combination of science with practice.

Before turning to another chapter, I beg leave to mention a very good instance of the way in which Englishmen have understood how to combine engineering with chemical manufacture. I have already spoken of the introduction into this country of the Leblanc process for the manufacture of one of the most important chemical products, carbonate of soda, or "alkali," in the parlance of trade. This process came over from France; but it had not been long employed in England before it was thoroughly modified in all particulars, and thus rendered more efficient and more remunerative. In no instance have the excellence of English methods, and their superiority over those used at that time on the Continent, been better proved than here. My own treatise on "Sulphuric Acid and Alkali" is, in its technological part, based mainly on what I had learned and practised during the twelve years of my residence in this country; and if that treatise has met with a favourable reception, as having proved useful to both British and non-British alkali makers, it is due to the circumstance just mentioned. But those methods, worked out during the second and third quarter of the last century, have had their day. A new process came up, which sapped the economical foundation of the Leblanc process. The history of this, the ammonia-soda process, has, strange to say, been directly contrary to so many others. It was invented by two Englishmen, Dyar and Hemming, who patented it in 1838, and who established the (very simple) chemical part of it in such manner that nothing really essential has been added since their time. But Dyar and Hemming did not succeed in the *practical* application of their invention, nor did their numerous successors meet with any better fortune, either in this country or elsewhere. It was reserved to a Belgian engineer, Ernest Solvay, to find the first economical solution of that problem, and this he achieved only after many years of patient work, and after sacrificing nearly all his means. Once he had gained his point, however, the economical superiority of the ammonia over the Leblanc process soon became evident. This was brought home to English manufacturers by the success of the firm of Brunner, Mond, and Co., which had acquired Solvay's English patent rights. The Leblanc process, and the enormous sums of money invested in it, seemed even then doomed to speedy extinction. But for a time, at least, this calamity was averted by the perseverance with which the British alkali makers kept making improvements in the Leblanc process, all calculated to cheapen it and lessen the nuisance connected with it. I cannot go into details on this point, but I wish to mention at least two things. One of these I have already spoken of in another connection—I mean the recovery of the sulphur from the alkali waste, where it had been the cause of an intolerable nuisance, and which now became the source of considerable profit. The second point is the substitution of machinery for manual labour in all stages of the process. It is only by means of these, along with a number of other improvements, that it has been made possible for the Leblanc process to survive to a certain extent. How much longer that is likely to continue I will not pause to speculate on. The prolongation of its life is due to the fact that in the first stage of the process an important acid is produced, which is not furnished by the ammonia process, viz., hydrochloric acid. Most of this is immediately converted into chlorine, which gas is used up for preparing very important articles of trade, viz., bleaching powder, bleach liquors, and chlorates. Of these, bleaching powder is a British invention, made by the Glasgow chemist, Tennant; but, apart from this, the manufacture of chlorine and of all chlorine products has been put on its practical basis almost entirely by English inventors, and has been developed more extensively in this country than anywhere else in the world. The processes worked out by Tennant and Dunlop at Glasgow, as well as by a host of others—amongst whom the names of Weldon and Deacon, in Lancashire, stand out prominently—have been copied for generations all the world over. The manufacture of chlorine products, which is not possible in the ammonia-soda process, has naturally given a new lease of life to the Leblanc process, at least in its first stage, which is the manufacture of salt-cake and hydrochloric acid. But, on the other hand, this last entrenchment of the Leblanc process is being vigorously assaulted from another quarter—by the electrolytic processes, which split up the alkaline chlorides directly, and in the simplest possible manner, into free chlorine and caustic alkali.

We are, in these days, so much accustomed to deal with electricity in its innumerable applications, that we are apt to forget how recent is the introduction of that force of Nature into practical chemistry. One of the finest heads among English alkali makers, whose grasp of the principles of science far surpassed that of most ordinary technical chemists, Dr. Ferdinand Hurter, pronounced himself, as late as 1888, decidedly against the commercial possibility of introducing electricity as an agent for manufacturing the cheaper class of chemicals. But within a very few years of that date the contrary had become an established and well-known fact, even in his own domain of alkali. True, in hardly any field have there been more failures to translate the results of science into economical manufacturing processes than in that of electricity; and even now it is only quite exceptionally that, wherever the electric current has to be produced by means of *steam*, electro-chemical methods can compete with the older ones for the manufacture of what is called "heavy chemicals." This is easily understood when we remember that about 90 per cent of the heat-value of coal, or its equivalent of energy, is lost in the circuitous routes of steam boiler, steam engine, and dynamo. But there are several ways in which the problem of obtaining cheaper electricity is being grappled with; and, if most of these have to be dismissed for the present, as belonging to the "music of the future," we have at least one which is a hard fact, and that is the generation of electricity by water-power. Unfortunately, in the British Isles the amount of available water-power is very limited in comparison with many other countries. It is a curious coincidence that those two European countries which are the greatest producers of coal, Great Britain and Germany, should be less favoured by Nature in respect of water-power than other countries which possess little or no stores of mineral fuel, as Sweden, Norway, Switzerland, France, Italy, and Spain. A very different condition of affairs obtains in the United States, where we find the greatest coal-fields combined with the greatest amount of water-power existing in any civilised country. It is impossible to shut one's eyes to the fact that the day will inevitably come when the coal-fields will be so far exhausted that all those industries which consume large amounts of mechanical energy will be forced to emigrate to countries where water-power is abundant.

No other substitute has, as yet, been found for generating force, and, indirectly, electricity. True, the energy given out by the descent of water in rivers is but a small fraction of that which is radiated upon the earth from

the sun, or of that which is developed by the play of the tides and the force of the wind, but no way has yet been found of utilising these other sources of energy, except to the slenderest extent. The harnessing of these natural agents belongs, so far as we can see, to the class of problems which will hardly be solved by our own generation, whatever developments the remoter future may bring. But of the water-power existing on this planet there is a large proportion which has never yet been touched, and this, as well as the water-power which has been already forced into the bonds of man, runs on for ever. This is, of course, an incalculable advantage over coal, which, by its use as fuel, is dissipated into the atmosphere in the shape of carbon dioxide, and thus altogether destroyed as a source of energy, since from carbon dioxide fresh fuel can only be generated by the intervention of solar energy, and this takes place at such a very slow rate that it cannot be taken into account in our economical consideration.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1907.

Sir Henry E. Roscoe, F.R.S., Past President, in the Chair.

Messrs. W. J. Bowis, L. M. Deane, E. W. L. Foxall, W. Godden, C. M. W. Grieb, and J. L. Simonsen were formally admitted Fellows of the Society.

Before commencing the business of the Society, Sir Henry Roscoe said that the Fellows would have learnt with great regret of the loss which their science, and especially French chemistry, had to deplore in the sudden and pathetic death of Marcelin Berthelot. This was not the occasion to dwell upon the important work which he had accomplished or on his noble character. These considerations would doubtless be fully dealt with hereafter. All that the Fellows of the Society now could do was to express their grief at his death and their sympathy with his family.

The Chairman also alluded with feeling to the death of their old Fellow, Prof. Warington.

Certificates were read for the first time in favour of Messrs. Kenneth Somerville Caldwell, B.Sc., Ph.D., St. Bartholomew's Hospital, E.C.; John Jacob Fox, 6, Alkham Road, Stamford Hill, N.; Joseph Henry Hall, B.Sc., 84, The Grove, Wandsworth, S.W.; Thomas Featherstone Harvey, 84, Henry Road, West Bridgford, Nottingham; Edward Houghton, Glenhyrst, 106, Salter-gate, Chesterfield; Carl Lewis, P.O. Box 36, Johannesburg, S. Africa; Herbert Victor Mitchell, 26, Brookfield Avenue, Walthamstow; Capt. George Colleymore Sturrock, R.A., Arubankad, Nilgiris, India; Sam Mortimer Sutcliffe, 4, Clive Place, Bradford.

Of the following papers, those marked * were read:—

*60. "*Synthesis of Polypeptides.*" By Emil Fischer.

Continuing his work on the synthesis of polypeptides the author has prepared an octadecapeptide containing fifteen glycocoll and three *l*-leucine residues.

Pentaglycylglycine was allowed to react with *d*-bromo-*iso*capronyldiglycylglycyl chloride, and the product so obtained was treated with ammonia with formation of *l*-leucyloctaglycylglycine. By a repetition of this series of reactions the octadecapeptide, *l*-leucyltriglycyl-*l*-leucyl-triglycyl-*l*-leucyloctaglycylglycine,—

$$NH_2{\cdot}CH(C_4H_9){\cdot}CO[NH{\cdot}CH_2{\cdot}CO]_3 \cdot NH{\cdot}CH(C_4H_9){\cdot}CO[NH{\cdot}CH_2{\cdot}CO]_3{\cdot}NH{\cdot}CH(C_4H_9){\cdot}CO[NH{\cdot}CH_2{\cdot}CO]_8{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

has been synthesised.

Discussion.

The Chairman said that he only voiced the feelings of the Society when he expressed his admiration for the interesting and remarkable lecture to which they had all listened with pleasure. In reciprocating to the full the words which had fallen from Professor Armstrong's lips as to the wonderful character of the researches which Professor Fischer had described, he remarked that whilst they looked upon these researches as typical of the great strides made in German chemical science, he ventured to think that Professor Fischer would agree with him when he said that he believed that the work done by the Fellows of our Chemical Society at the present time would bear not unfavourable comparison, both as to quality and quantity, with that which is now being carried out in Germany. Indeed, when he looked back to the early years of the Society, as his friend Sir William Perkin and he could do, and remembered the progress which it had made, the activity which the Fellows of the Society had shown in recent years in advancing the progress of their science struck him as most remarkable, and this in spite of the many drawbacks which have often been said to discourage original research in England. We could not, indeed, vie with Germany in the special department of research which had just been laid before the Society, and this for a very simple reason, that there was only one Emil Fischer.

*61. "*Organic Derivatives of Silicon.* Part III. dl-*Benzylmethylethylpropylsilicane and Experiments on the Resolution of its Sulphonic Derivative,*" By Frederic Stanley Kipping.

dl-Benzylmethylethylpropylsilicane, SiMeEtPrBz (*Proc.*, 1905, xxi., 65), is sulphonated by sulphuric acid at about 130°, yielding a mixture of acids of which two were isolated in the form of their *l*-menthylamine salts.

Analyses of one of these salts seem to show that it is derived from *benzylethylpropylsilicolsulphonic acid*, and has the formula $EtPrSi(OH){\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H,C_{10}H_{21}N$, but as it is formed in small amount only it has not been very thoroughly investigated; the formation of such an acid from the silicohydrocarbon would necessitate the hydrolytic separation of the methyl group in a manner similar to that in which the phenyl group is displaced on sulphonating phenylbenzylethylpropylsilicane (*Trans.*, 1907, xci., 224). The salt crystallises in prisms, and melts at 210—212°.

The second *l*-menthylamine salt isolated from the mixture is derived from dl-*benzylmethylethylpropyl-silicanesulphonic acid*, and has the formula $SiMeEtPr{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H,C_{10}H_{21}N$. This compound is much more easily obtained from the product of the sulphonation of benzylmethylethylpropylsilicane with chlorosulphonic acid. It crystallises best ($+2H_2O$) from wet, light petroleum, and when dehydrated melts at 121—123°.

The *l-menthylamine*, *quinine*, *cinchonidine*, *cinchonine*, *narcotine*, and several other salts of this *dl*-silicanesulphonic acid have been crystallised fractionally under various conditions, but without the faintest indication of a resolution of the acid having been observed.

*62. "*The Reduction of Carbon Dioxide to Formaldehyde in Aqueous Solution.*" By Henry John Horstman Fenton.

The author finds that by the action of metallic magnesium, under appropriate conditions, on an aqueous solution of carbon dioxide, recognisable quantities of formaldehyde can be obtained, and that the amounts are considerably increased if weak bases, such as ammonia, aniline, phenylhydrazine, or aluminium hydroxide are also present.

Further, it is found that formic acid may readily be reduced, in part at any rate, to formaldehyde by the action of magnesium, so that the desired reduction of carbon dioxide may be effected also in two stages, with formic acid as the intermediate product.

*63. "*The Mechanism of the Rusting of Iron.*" By Gerald Tattersall Moody.

The author has previously shown that the presence of acid is essential for rusting to occur. The following experiments enables the exact mechanism of the production of rust to be visualised:—In the bottom of a glass cylinder are placed some rods of bright iron such as French nails. These are only loosely packed, for the most part heads upward, and are so arranged that some of them remain vertical whilst others occupy inclined positions. Recently boiled distilled water is then poured into the cylinder until it stands about one and a-half inches above the heads of the nails. The mouth of the cylinder is loosely closed with a sheet of paper so as to exclude dust and at the same time to allow free access of air to the water, whereby carbonic acid and oxygen are absorbed. In the course of twenty-four hours the water shows signs of becoming turbid, and shortly afterwards a copious separation of brown particles from the solution is distinctly observed. These brown particles are continuously formed, and gradually settle on the heads of the nails, and on the upper parts only of those nails which are inclined. The under parts of the inclined nails and the vertical nails remain bright, no general corrosion of the surfaces being observable. At the end of seven days a thick layer of hydrated ferric oxide has collected on the upper surfaces of the nails, and also on the bottom of the cylinder. If a sheet of hardened filter-paper or some other material which allows of diffusion be placed in a horizontal position immediately over the nails at the beginning of the experiment, the rust which separates from the solution above it gradually collects on its upper surface and eventually forms a thick layer.

The separation of the rust from the water and its non-formation on the surface of the iron can be explained only as an oxidation of ferrous iron actually in solution. This is in strict accordance with the experimental evidence already advanced, and shows that, in rusting, iron is first dissolved with formation of ferrous salt which subsequently oxidises to rust.

Discussion.

The Chairman remarked that all those present must be much struck by the extremely simple and convincing experiments which the author had described, showing that the first step towards the rusting of iron was that the metal entered into solution in the liquid. He ventured to doubt, however, whether the author had even now got to the bottom of the subject, simple though it apparently was, because he had not explained how the solution of the metal was effected, whether this solution occurred in presence of carbonic acid only or whether in its absence.

Dr. Moody said that he had already described experiments which showed conclusively that the presence of acid is essential for rusting to occur (*Trans.*, 1906, lxxxix., 720). In absence of acid, pure iron was allowed to remain in contact with water and oxygen for several weeks without even one speck of rust being formed, and without the iron undergoing any change either in appearance or in weight. It was specially noteworthy that when pure iron was placed in a dilute solution of hydrogen peroxide free from acid, no oxidation or other change in the iron occurred, although oxygen was freely evolved from every part of the immersed metal. In this way the indifference of iron towards oxygen in presence of water could be easily and conclusively demonstrated. In the experiment he had shown the Society that evening, the iron was undoubtedly dissolved by carbonic acid, and the ferrous bicarbonate thus formed was converted into rust by oxygen, which, simultaneously with the carbonic acid, diffused into the solution from the atmosphere.

*64. "*Influence of Non-electrolytes and Electrolytes on the Solubility of Sparingly Soluble Gases in Water. The Question of Hydrates in Solution.*" By James Charles Philip.

It is suggested that the influence of non-electrolytes and electrolytes on the solubility of gases may be adequately interpreted by reference to two factors. Firstly, it may be supposed that the non-electrolyte or electrolyte takes no part in the absorption, and accordingly the standard absorbing volume should be not 1 cc. or 1 litre of the solution, but that volume of the solution which contains 1 grm. or 1000 grms. of the pure solvent. Secondly, hydration of the non-electrolyte or electrolyte may occur, and it may be supposed that the solvent which is thus attached is no longer free to absorb the gas. These suggestions have been tested with satisfactory results by reference to available experimental data, and the values found for the average molecular hydration of dissolved salts are in fair agreement with the values reached by other and widely different methods.

Discussion.

Sir William Ramsay asked whether it must not be held that both the solvent and the solute take part in dissolving a gas. For example, a solution of sugar in water is a mixture of liquid sugar and liquid water, and it might be supposed that hydrogen would dissolve in both water and in sugar according to its solubility in each and to their relative amount.

Mr. R. J. Caldwell drew attention to the fact that Euler and others had recognised that the absorption coefficients of the permanent gases, as well as the solubility of ethyl acetate, are equally affected by the presence of dissolved solids. It had long been clear to him that this regularity could be accounted for by assuming that a diminution of the amount of free water was caused by the formation of hydrates of the dissolved substance; most of the material had been collected for a communication on the subject. From the very accurate values given by Winkler for the solubility of oxygen, making due allowance for the fact that Winkler used volume-normal solutions, he had calculated that the average degree of hydration of calcium chloride in a solution of grm.-molecular strength (weight-normal) was in the ratio $CaCl_2 : 21H_2O$. This result is in accord with the value $CaCl_2 : 22H_2O$ he had obtained by the sugar inversion method; in the case of other salts, a like agreement had been found. It was difficult to see how such agreements could be reconciled with the ionic dissociation hypothesis.

Dr. Philip said that it was certainly possible that hydrogen was soluble to some extent in chloral hydrate and sucrose, but it appeared unlikely in view of the fact that the average molecular hydration calculated on the basis of the two factors suggested in the paper agreed with values obtained by methods into which the question of solubility of hydrogen in these substances could not possibly enter.

The view that hydrates exist in aqueous solutions of electrolytes was not inconsistent with a general adherence to the ionic theory.

*65. "*A New Class of Organo-metallic Compounds.* (Preliminary Notice). *Trimethylplatinimethyl Hydroxide and its Salts.*" By William Jackson Pope and Stanley John Peachy.

No alkyl compounds of metals belonging to Group 8 of the Periodic Table have hitherto been described. The authors find that the chlorides, or in some cases the oxides, of iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum, belonging to Group 8, and of gold, belonging to Group 1, react vigorously with magnesium methyl iodide; they desire to reserve the study of the action of Grignard's reagent on compounds of the metals named.

Trimethylplatinimethyl iodide, $(CH_3)_3PtI$, is formed by the action of platinic chloride dissolved in ether on magnesium methyl iodide in ethereal benzene solution; after treating with water and extracting with benzene, the benzene solution yields the new compound on evaporation. It crystallises in straw-yellow plates, is not volatile, and decomposes on heating with slight explosion; it is very stable towards reagents, and is not attacked in the cold

by strong caustic alkalis, alkali sulphides, or by nitric, hydrochloric, and sulphuric acids. It is not further acted on by magnesium methyl iodide. On boiling for several hours with silver hydroxide in a moist mixture of benzene and acetone, it is converted into *trimethylplatinimethyl hydroxide*, $(CH_3)_3Pt{\cdot}OH$; this substance is insoluble in water, gives no alkaline reaction with litmus, and crystallises in colourless rhombic dodecahedra belonging to the cubic system.

Trimethylplatinimethyl nitrate, $(CH_3)_3Pt{\cdot}NO_3$, obtained by dissolving the hydroxide in nitric acid, crystallises in colourless plates, and is freely soluble in water. On adding an alkali chloride to its aqueous solution, *trimethylplatinimethyl chloride*, $(CH_3)_3PtCl$, is precipitated; this salt crystallises from chloroform in colourless rhombic dodecahedra belonging to the cubic system. In a similar manner a number of other salts have been prepared, including the *bromide* and the *cyanide*; the latter is hydrolysed on heating with caustic potash with evolution of ammonia.

DISCUSSION.

The CHAIRMAN congratulated the authors on having opened out an entirely new branch of investigation which might indeed be said to be a wonderful "find."

(To be continued).

FARADAY SOCIETY.

Ordinary Meeting, March 19th, 1907.

Dr. T. MARTIN LOWRY in the Chair.

The following nominations for the Officers and Council to be elected at the forthcoming Annual General Meeting were announced:—

President—Sir William Perkin, F.R.S.

Vice-Presidents—G. T. Beilby, F.R.S.; R. A. Hadfield; Prof. W. Hittorf, Geh. Reg.-Rat.; Sir William Huggins, O.M., K.C.B., F.R.S; Prof. A. K. Huntington; Prof. A. Schuster, F.R.S.; Prof. J. J. Thomson, F.R.S.

Treasurer—F. Mollwo Perkin, Ph.D.

Council—A. C. Claudet, M.I.M.M.; S. Z. de Ferranti, M.I.E.E.; F. W. Harbord, F.I.C.; R. S. Hutton, D.Sc.; T. M. Lowry, D.Sc.; W. M. Morrison, M.Inst.C.E.; James Swinburne, F.R.S.; N. T. M. Wilsmore, M.Sc.; Prof. E. Wilson; J. L. F. Nogel, M.I.E.E.

A paper by Mr. H. NUTTON and Mr. H. D. LAW on "*The Potential of Hydrogen liberated from Metallic Surfaces*," was read in abstract by Mr. NUTTON:

The paper is chiefly concerned with the chemical reducing power of hydrogen when liberated from the surface of various metallic electrodes, and also the retarding action caused by the presence of small quantities of metallic salts. The metals are arranged in the following order: mercury, lead, cadmium, tin, silver, bismuth, gold, nickel, platinum (black), the first-mentioned metal being the most capable of bringing about the reduction of a compound not readily attacked; platinised platinum, on the other hand, possesses this property in the lowest degree. Zinc as a reducer behaves in a very irregular manner; both copper and platinum (black) show a remarkable activity in the reduction of aromatic aldehydes, and iron and aluminium are variable. It was hoped by a careful study of the electrode potentials that it might be possible to differentiate between the purely chemical changes and those which were due to physical causes.

The E.M.F. between the cathode and the hydrogen electrode was measured on the Clark Fisher "compensating potentiometer" reading to one-tenth millivolt. The current was read on a standard millivoltmeter shunted to read milliamperes. The cathode solution was contained in a carefully cleaned porous pot fitted with a rubber stopper having three outlets, the cathode being fixed in one by means of sealing wax, and thus being easily removed. Another hole in the stopper contained a capillary tube connected with the hydrogen electrode which was arranged to be close to the metallic cathode. When possible the cathodes were bent in the form of a cylinder and had a superficial area of 20 sq. centimetres on one side. The conclusions arrived at are briefly as follows:—The supertension of one and the same metal is not a fixed quantity, being influenced by the physical and chemical nature of the surface. Film formations have also a large influence. Chemical reactions are greatly increased by raising the supertension. The nature of the electrolyte can completely change the nature of the chemical reaction without any corresponding change in the supertension. The supertension gives but a small indication of catalytic action. The fall of potential on the addition of a depolariser is only a rough guide to the nature of the reduction which is taking place.

Mr. JOHN RHODIN drew attention to the effect of barometric pressure on the liberation of hydrogen on the cathode. The question of the potential of hydrogen had an important bearing on the dissolution velocity of metals, and here pressure had a very marked influence.

Mr. N. T. M. WILSMORE said that the authors had shown that the connection between supertension and reducing power that had been claimed by Nernst did not really exist.

Mr. H. D. LAW thought that, in view of the enormous pressure of the hydrogen on the cathode, any change of barometric pressure was not likely to be of effect. He inclined to the view that many metals existed in two forms, one with a high and one with a low supertension. The result of the paper was to show that supertension was a very variable quantity, and much more work remained to be done on the subject.

Mr. N. T. M. WILSMORE then read a paper, written conjointly with Mr. F. M. G. JOHNSON, on "*Electrode Potentials in Liquid Ammonia*."

The measurements of electrode potentials in liquid ammonia were undertaken with a view to the determination of the free energy of formation of a series of metallic salts, and thereby to compare the relative affinities of the corresponding metallic elements under conditions differing as much as possible from those obtaining in the case of measurements in aqueous solutions. To this end the electrode potentials of the metals against solutions of their salts of known strength were measured against a standard electrode (cadmium in a saturated solution of cadmium nitrate). The results are given in the paper in tabular form.

In order to obtain values for the single electrode potentials, the "standard" electrode employed was measured directly against the $n/10$ calomel electrode, and the P.D. thus found was used to calculate the E.M.F.'s tabulated in the paper. (See accompanying table).

For comparison, the corresponding "electrolytic potentials" for aqueous solutions are added in the tables. Owing to lack of conductivity data, however, it was not possible to reduce the electrode potentials in ammonia to electrolytic potentials referred to unit ionic concentration. The research is thus, in a sense, incomplete.

Mr. JOHN G. A. RHODIN then read a paper entitled "*The Impedance of Solutes in Solvents as manifested by Osmotic Pressure*."

The author's object is to substitute for the theory of van't Hoff, the main objection to which, in his opinion, is the direction of pressure, a theory which regards the solvent—and not the solute—as the source of the energy manifested in osmotic pressure experiments. The presence of a solute in a solvent diminishes the potential energy of the latter; there is, therefore, a flow of energy across the semi-permeable membrane from the solvent to the solution inside the membrane. The "osmotic pressure" is thus a potential pressure, made actual by the transformation of the excessive potential energy of the solvent

Metal.	Electrolyte.	E.M.F. in liquid NH_3.	E.P. in aqueous solution.	Difference. For *n*/10.	Difference. For *n*/100.
K	KI *n*/10	+2·64	+3·20	−0·56	
Na	NaCl *n* 10..	+2·63	+2·82	−0·19	
Na	$NaNO_3$ *n*/10	+2·61	+2·82	−0·21	
Ca	$Ca(NO_3)_2,4H_2O$ *n*/10	+2·53	+2·56	−0·03	
Mg	MgI_2 *n*/100	+2·31	+2·54 +1·49		−0·23 +0·82
NH_4	NH_4NO_3 *n*/10	+1·96			
Zn	$Zn(NO_3)_2,6H_2O$ *n* 100	+1·424	+0·770		+0·65
Zn	$Zn(NO_3)_2,6H_2O$ *n* 10	+1·401	+0·770	+0·63	
Cd	$Cd(NO_3)_2,4H_2O$ *n* 100	+1·134	+0·420		0·71
Cd	$Cd(NO_3)_2,4H_2O$ *n*/10	+1·095	+0·420	0·68	
Ni	$Ni(NO_3)_2,6H_2O$ *n* 10	+0·548	+0·228	0·32	
Pb	$Pb(NO_3)_2$ *n*/100	+0·553	+0·148		0·41
Pb	$Pb(NO_3)_2$ *n*/10	+0·533	+0·148	0·39	
Cu	$Cu(NO_3)_2,3H_2O$ *n*/100	+0·47	−0·329		0·80
Cu	$Cu(NO_3)_2,3H_2O$ *n*/10	+0·35	−0·329	0·68	
Cu	$Cu(NO_3)_2,3H_2O$ *n*/1	+0·37	−0·329		
Hg	HgI_2 *n*/100	+0·181	−0·750		0·93
Hg	HgI_2 *n*/10	+0·153	−0·750	0·90	
Ag	AgI *n* 100..	+0·221	−0·771		0·99
Ag	AgI *n*/10	+0·163	−0·771	0·93	
Ag	$AgNO_3$ *n*/100	+0·116	−0·771		0·89
Ag	$AgNO_3$ *n*/10	+0·085	−0·771	0·86	

on the one side of the semi-permeable membrane, by absorption of exterior heat energy. Hence the time required is a function of the alteration of the volume of the solution on the other side of the membrane, and accurate and speedy methods of mensuration must involve the keeping of this volume as nearly constant as possible.

To explain the action of semi-permeable membranes, the author imagines these—and colloids generally—to be composed of radial filaments, emanating from a common centre. The structure is coarse compared with that of the solvent, but the cilia impede the motion of the molecules of the latter. In an osmotic experiment the stronger bombardment on the solvent side polarises the filaments into cones, and a kind of Bunsen valve is thus produced.

Dr. T. M. Lowry said the "sieve" theory of the membrane, which the author seemed to advocate, was now generally abandoned, the view that the action was one of selective solubility being substituted.

Dr. T. Slater Price communicated Part II. of a paper entitled "*The Electrolytic Deposition of Zinc, using Rotating Electrodes.*"

The effect of the addition of various electrolytes on the electrolytic deposition of zinc, using a rotating cathode and the apparatus described in the previous paper, has been investigated. In all the experiments the cathode was silvered before the zinc was deposited. Excellent results were obtained, using 2 grms. of sodium sulphate and 1 grm. of sodium acetate for each grm. of crystallised zinc sulphate, the addition of free acetic acid being unnecessary. The number of revolutions per minute of the cathode was 600 to 700, and the time of deposition was fourteen minutes. Satisfactory, but slightly high results, were also obtained when the following electrolytes were used: (1) 2 to 5 cc. concentrated ammonia, (2) 4 grms. caustic soda, (3) 3 grms. sodium acetate. The amount of zinc sulphate taken for each determination was 1 grm., and the solutions were electrolysed in the cold; if they were heated to boiling-point before the electrolysis was commenced the results were unsatisfactory. Neither ammonium acetate nor sodium sulphate is a satisfactory electrolyte.

Unless the cathode was coated with either silver or copper before the zinc was deposited high results were obtained, and it was difficult to get all the zinc out of the solution. When a rotating cathode is used, the zinc does not alloy with the platinum if deposited directly on to it (*cf.* Medway, *Amer. Journ. Sci.*, 1904, [4], xviii., 56).

The modification of Kollock and Smith's method (rotating anode and mercury cathode), which was suggested in the first paper, has not been found to be as satisfactory as at first trial it seemed to be. Considerable experience and very careful manipulation are required before good results can be obtained.

A thorough examination of Kollock and Smith's own method has shown it to give low results for zinc, both zinc and mercury being lost in the washing to which the amalgam is subjected; a little zinc dissolves as hydrate in the wash-water, and some mercury is either mechanically carried away or else chemically dissolved.

NOTICES OF BOOKS.

Photography for Students of Physics and Chemistry. By Louis Derr, M.A., S.B. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1906.

This volume is based upon the author's lectures on Photography delivered at the Massachusetts Institute of Technology, and it occupies a unique position among handbooks dealing with the subject. It is in no sense a complete treatise for the use of advanced students, nor is it a popular account of photographic manipulation, designed for the worker without scientific knowledge, but it attempts to describe the processes with special reference to the principles involved, and to explain the details for the benefit of those who have some acquaintance with the elements of physics and chemistry, and who wish to understand the phenomena which lie at the basis of the operations. The earlier chapters discuss elementary optics and explain the function of the lens, methods of testing lenses, and aberration. The diaphragm and its use are next considered, and a chapter is devoted to the camera and its accessories. The chemistry of the process is then taken up and the reactions involved in development, intensification, and reduction are fully and carefully explained. The making of lantern slides is also described, and the book ends with a short and perhaps somewhat inadequate account of colour photography, which in a book of this kind might with advantage have been treated in rather greater detail.

Handbuch der gesammten Thonwaaren-industrie. ("Handbook of the Clay Industries.") By Bruno Kerl. Third Edition, prepared by Eduard Cramer and Dr. Hermann Hecht. Braunschweig: Friedrich Vieweg und Sohn. 1907.

This comprehensive work is intended for the use both of technical students and of specialists, and all those who have any connection with the clay industries, and who wish to have at their disposal the latest information concerning practically any branch of these industries, will find it a valuable possession. As in the earlier editions, the first part deals with the general principles involved, and the second treats of the manufacture of various articles and products in detail. The third edition has been enlarged to more than twice the size of the original, and contains double the number of illustrations, and will rank as one of the most thorough and complete text-books extant on the subject.

La Moderna Teoria dei Fenomeni Fisici. ("Modern Theory of Physical Phenomena.") Third Edition. By Augusto Righi. Bologna: Ditta Nicola Zanichelli. 1907.

Although it is not very long since the second edition of Prof. Righi's interesting work appeared, so much fundamental work has been done with regard to the phenomena of radio-activity, and recent theoretical developments have been of such great importance, that the third edition contains a great deal of new matter. A chapter is added on the atomic transformations of the radio-active bodies, and the bibliography has been brought down to the year 1906. As an elementary discussion of modern theories this book is excellent; it is written in popular style, and yet is accurate in every respect, and both the general reader and the student with an elemeutary knowledge of physics and chemistry will find that it gives an interesting and clear account of the principal facts upon which the electron theory is based.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 11, March 18, 1907.

A Property of Platinum Amalgam.—H. Moissan.—Pure mercury shaken with water, as is well known, forms no mixture with it; but an amalgam of mercury and platinum after being shaken for a few seconds with water forms a semi-solid mass, of the consistency of butter, and of about five times the volume of the original amalgam. This emulsion is stable, and exhibits no change after standing for a year; it resists the action of heat and of cold. Microscopic examination shows droplets of water disseminated through the mass, giving it a cellular appearance. Copper, silver, and gold amalgams do not form emulsions with water. Platinum amalgam forms emulsions with other liquids also, such as sulphuric acid, solutions of ammonia, ammonium chloride, sodium chloride, glycerin, acetone, alcohol, ether, carbon tetrachloride, chloroform. All are stable. Emulsification is also produced when mercury is shaken with water to which a 10 per cent solution of platinum chloride has been added.

Alloys of Nickel and Tin.—Em. Vigouroux.—The author gives some results of his researches upon pure bronzes, in which the red copper has been replaced by white copper or nickel, and in all cases the alloys contain more than 66 per cent tin. The analyses of three operations give as the composition of the alloys 73·64, 83·65, and 92·71 per cent tin respectively, the rest being represented by nickel in each case. They all possess the usual non-magnetic character.

The Arsenites and Arseniates of Rubidium.—A. Bouchonnet.—The author describes the preparation of certain oxygen compounds of arsenic with rubidium and cæsium hitherto not made known. 1. *Rubidium Meta-arsenite*, AsO_2Rb.—Obtained by dissolving in water the molecular weights of arsenious anhydride and rubidium carbonate, $As_2O_3 + Rb_2CO_3 \quad 2AsO_2Rb + CO_2 + H_2O$. This is a syrupy mass which can be dehydrated on a porous plate *in vacuo* to a white amorphous powder. It possesses the general characteristics of the arsenites, reducing potassium permanganate and chromic acid. 2. *The Monobasic Arseniate*, AsO_4RbH_2.—Obtained (*a*) by melting equal parts of arsenious anhydride and rubidium nitrate, dissolving in water, filtering, and evaporating *in vacuo*; (*b*) by neutralising an aqueous solution of rubidium carbonate with arsenic acid, using methyl-orange as indicator, then crystallising as before. 3. *The Dibasic Arseniate*, AsO_4Rb_2H.—Prepared by weighing out of contact with the air 5 grms. of pure rubidium hydrate and 11 grms. of the monobasic arseniate, weights calculated from the formula $AsO_4RbH_2 + RbOH = AsO_4Rb_2H + H_2O$. These are mixed in aqueous solution and evaporated *in vacuo*. The crystals, consisting of white plates, lose their water of crystallisation, changing to the pyroarseniate, $As_2O_7Rb_4$, under the action of heat. On further heating the latter changes to the meta-arseniate, AsO_3Rb. 4. *The Tribasic Arseniate*, AsO_4Rb_3.—Obtained by neutralising an aqueous solution of rubidium hydrate by arsenic acid. Trirubidic arseniate crystallises with difficulty. It is necessary to evaporate in the presence of caustic potash, placing the moist crystals finally on a porous plate and leaving them for several days in presence of phosphoric anhydride.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 2, 1907.

Pentaphenyl-ethane and Hexaphenyl-ethane.—A. E. Tschitschibabin.—The author has shown that in an atmosphere of carbon dioxide pentaphenyl-ethane melts at 178—179°. Decomposition always occurs at the melting-point. In air it possesses no sharp melting-point, but gradually decomposes on warming, oxidation taking place. At high temperatures, both as such and also in nitrobenzene solution, it absorbs the oxygen of the air energetically. On warming it splits up into *sym*-tetraphenyl-ethane and hexaphenyl-ethane (triphenyl methyl), and the latter (and in certain circumstances the former also) is then oxidised by the oxygen of the atmosphere. When warmed with hydrochloric acid in benzene solution in absence of air, at 150° the substance is converted into *sym*-tetraphenyl-ethane, triphenyl-methane, and triphenylchlor-methane, and is thus very labile. These experiments show that triphenylmethyl is probably hexaphenyl-ethane, Schmidlin's "hexaphenyl-ethane" is possibly a somewhat impure tetraphenyl-methane, the result of the condensation $(C_6H_5)_3CCl + C_6H_6 = (C_6H_5)_4C + HCl$.

Detection of Salts of Sulphurous Acid in presence of Thiosulphates and Thionates.—E. Votocek.—The author's method is based upon the observation that solutions of normal sulphurous acid salts react almost instantaneously with dilute solutions of many dye-stuffs of the triphenylmethane series (fuchsine, malachite-green, &c.). Decolorisation ensues immediately on mixing the solutions, for sulphites of the colour bases are formed which are practically colourless in dilute solution. If a sufficient amount of aldehyde is added to the colourless solution (preferably an aqueous solution of acetaldehyde) an intense violet colour is produced, while with green dye-stuffs, *e.g.*, malachite-green, a green coloration appears. Thiosulphates, di-, tri-, and tetra-thionates do not decolorise the above solution, and thus this reaction can be used to detect sulphites in presence of these salts. Bicarbonates,

sulphydrates, phosphates, &c., do not affect the reaction, but mono- and polysulphides behave like the sulphites; hence sulphur ions must be removed by means of zinc or cadmium ions. A mixture of fuchsine and malachite-green is the best to use, containing three volumes of fuchsine solution (0·25 grm. fuchsine to 1 litre of water) to one volume of malachite-green solution of the same strength. If the solution to be tested contains free alkali this must be converted into bicarbonate by means of a current of carbon dioxide. If the solution is acid pure bicarbonate must be added. The test is very sensitive; an aqueous solution containing only 0·00006 grm. of sulphurous acid in 1 cc. instantly decolorises the dye solution, and shows a violet coloration on addition of acetaldehyde. The following scheme shows how the test may be applied:—

I. The solution—
- (*a*) Decolorises the fuchsine malachite reagent, and becomes violet with acetaldehyde;
- (*b*) Gives a violet coloration with alkaline sodium nitroprusside solution;
- (*c*) After shaking with $CdCO_3$, filtering, and saturating with CO_2, the dye solution is not decolorised, nor is S separated on acidifying.

It contains poly- or monosulphides, but no sulphite.

II. The solution—
- (*a*) Does not decolorise the dye reagent;
- (*b*) Gives no coloration with sodium nitroprusside solution.

It may contain thiosulphate, or di-, tri-, or tetrathionate.

III. The solution—
- (*a*) Decolorises the dye reagent;
- (*b*) Gives no coloration with alkaline sodium nitroprusside solution.

It contains sulphite and thiosulphate.

IV. The solution—
- (*a*) Decolorises the dye reagent;
- (*b*) Gives a violet coloration with alkaline sodium nitroprusside solution;
- (*c*) Treated as in I. (*c*), decolorises the dye-stuff, but gives no sulphur with acids.

It contains monosulphide and sulphite.

V. The solution—
- (*a*) Gives a violet coloration with alkaline sodium nitroprusside solution;
- (*b*) Decolorises the dye solution;
- (*c*) Treated as in I. (*c*), does not decolorise the dye solution.

It contains monosulphide and thiosulphate.

VI. The solution—
- (*a*) Decolorises the dye solution;
- (*b*) Gives a violet coloration with alkaline sodium nitroprusside solution;
- (*c*) Treated as in I. (*c*), decolorises the dye solution, and gives S with acids.

It contains monosulphide, sulphite, and thiosulphate.

The same method can be used for detecting sulphurous acid in presence of sulphuretted hydrogen in the gaseous state. The mixture of gases must be led through a U-tube with hot cadmium sulphate solution, and then through a U-tube containing the fuchsine malachite-green solution to which some sodium bicarbonate has been added. If this is decolorised and a violet coloration subsequently produced with acetaldehyde, sulphurous acid is present. Moreover, the same reagent may be used to distinguish dilute solutions of sulphydrate and sulphides, for the former do not decolorise the solution, while the latter do.

Solubility of the Alkaline Earths in their Fused Chlorides.—Kurt Arndt.—When calcium oxide is dissolved in fused calcium chloride and the melt allowed to solidify, it is found that lime begins to separate at 800°, and that at 800° at the most 7·0 per cent of calcium oxide is dissolved in the saturated melt. This is equivalent to 7·5 per cent CaO to 100 grms. $CaCl_2$. The solidification point of calcium chloride is not lowered by dissolving lime in it, which shows that calcium oxide forms a solid solution with the chloride. Similar experiments were performed with the oxides of strontium and barium, and the results may be stated as follows:—1 mol. of CaO dissolves in 7 mols. $CaCl_2$; 1 mol. of SrO dissolves in 3 mols. $SrCl_2$; 1 mol. of BaO dissolves in 2 mols. $BaCl_2$. The effect of the addition of fluor-spar on the solubility of lime in fused calcium chloride was then investigated. Fifty-four grms. of calcium chloride were fused with 6 grms. of calcium fluoride, and 7 grms. of calcium oxide were added; the solubility of the oxide was then found to be almost unaltered by the fluoride.

Hydrazoic Acid.—L. M. Dennis and Helen Isham.—The authors have prepared anhydrous hydrazoic acid by adding dilute sulphuric acid (two parts acid to one part water) to potassium trinitride in a current of dry carbon dioxide. The free acid was dried by passing it through calcium chloride tubes and collected in a vessel which was surrounded by a Dewar's vessel containing liquid air. The whole apparatus was placed behind a screen of thick plate-glass before which were wooden walls, and other precautions were taken to ensure the safety of the operator. The temperature was ascertained by means of a pyrometer. The acid yielded a white crystalline mass which slowly melted when the liquid air was allowed to evaporate. The melting-point was found to be $-80°$ and the boiling-point about 37°. The acid is a colourless mobile liquid which is heavier than water and probably has a high surface tension. At ordinary temperatures it is apparently quite stable, but explodes readily and with great violence if it is shaken or strongly heated. The authors succeeded in analysing the anhydrous acid, and found its vapour density; the latter at a temperature only 25° above the boiling-point indicates that the compound has the monomolecular formula HN_3.

MISCELLANEOUS.

Royal Institution.—On Tuesday, April 9th, at 3 o'clock, Professor G. H. Bryan, F.R.S., will begin a course of two lectures on "Wings and Aeroplanes"; on Thursday, April 11th, at 3 o'clock, Professor H. A. Miers, F.R.S., will commence a course of two lectures on "The Birth and Affinities of Crystals"; and on Saturday, April 13th, at the same hour, Professor Silvanus P. Thompson, F.R.S., will begin a course of three lectures on "Studies in Magnetism" (The Tyndall Lectures). The Friday Evening Discourse on April 12th will be delivered by Professor A. H. Church, F.R.S., the subject being "Conservation of Historic Buildings and Frescoes," and on April 19th by Professor C. S. Sherrington on "Nerve as a Master of Muscle."

MEETINGS FOR THE WEEK.

MONDAY, 8th.—Society of Chemical Industry, 8. "Observations on Cotton and Nitrated Cotton," by H. de Mosenthal.

TUESDAY, 9th.—Royal Institution 3. "Wings and Aeroplanes," by Prof. G. H. Bryan, F.R.S., &c.

WEDNESDAY, 10th.—Society of Arts, 8. "Arts and Industries in Hungary in Ancient and Modern Days," by Louis Felberman.

—— Society of Public Analysts, 8. "Bacterial Estimation of Phenol and Cresol," by M. Wynter Blyth and L. Goodbao. "New Method for the Estimation of Tartaric Acid," by A. C. Chapman and P. Whitteridge. "Detection of Cocoanut Oil in Butter," by E. Hinks.

THURSDAY, 11th.—Royal Institution, 3. "The Birth and Affinities of Crystals," by Prof. H. A. Miers, F.R.S., &c.

FRIDAY, 12th.—Royal Institution, 9. "Conservation of Historic Buildings and Frescoes" (with Experimental Illustrations), by Prof. A. H. Church, F.R.S.

SATURDAY, 13th.—Royal Institution, 3. (The Tyndall Lectures). "Studies in Magnetism," by Prof. Silvanus P. Thompson, F.R.S.

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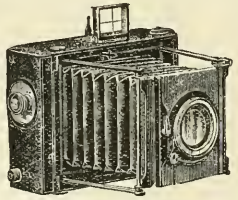

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SOME EXPERIMENTS WITH CHROMIUM TRIOXIDE.

By MAURICE R. READ.

1. When chromium trioxide is introduced on the end of a platinum-wire into a jet of burning hydrogen or the non-luminous flame of a Bunsen burner, the conversion of the trioxide into the green chromic oxide is accompanied by the production of a white light of dazzling brilliancy. The luminosity of the flash is little short of that emitted by burning magnesium, though the colour is an almost pure white instead of bluish white. The substance changes in tint from red to grey before the flash. That CrO_3 decomposes with some violence if heated to a temperature slightly above its melting-point is well known, but the writer has seen no reference to this distinctive behaviour of the oxide when introduced into a flame.

2. If the trioxide is gently heated in a stream of coal-gas or hydrogen a somewhat brilliant combustion ensues, three different residues remaining in the boat; a grey semi-fused powder in the central portions, a purplish substance at the ends, and beneath these a layer of the green sesquioxide of chromium. In the coal-gas experiment, the flame of a Bunsen burner, in which the issuing gas was burnt, at first exhibited luminosity, owing, no doubt, to escaping oxygen, but at the moment of the combustion in the tube the lividity disappeared. Similar effects were observed in the experiment in which hydrogen replaced the coal-gas.

3. Heated in a like manner in a stream of carbon dioxide, chromium trioxide yields, besides vapours imparting luminosity to a Bunsen flame, a small quantity of a brownish purple body resembling that already mentioned, but there is no combustion within the tube. The result of heating the trioxide in a stream of nitrogen is similar, but a dull bluish residue, dark green beneath, was obtained in place of the purplish substance formed in the previous experiments.

4. The vapour of chromyl chloride, passed into a non-luminous Bunsen flame, imparts to it a very characteristic livid whiteness, resembling that produced by the vapour of CrO_3.

5. The purple, brownish purple, and bluish residues above described, introduced on a platinum-wire into a non-luminous gas flame, emitted a brilliant light, closely similar to that caused by chromium trioxide.

The question has arisen whether the dark coloured residue obtained, which behaves in such a characteristic manner in a non-luminous flame, is possibly the "violet" oxide of chromium, Cr_5O_9, mentioned in Roscoe and Schorlemmer's "Chemistry," 'The Metals,' 3rd Ed., 1897, p. 836, or is it CrO_2 tinted by the presence of small quantities of undecomposed CrO_3?

On the former supposition (as suggested to me by Mr. E. G. Clayton, in whose laboratory I have made these experiments) such reactions as the following might have occurred:—

$$(a) \qquad 3CrO_3 = Cr_2O_3.CrO_3 + 3O.$$
(Dioxide)

$$(b) \quad Cr_2O_3.CrO_3 + 2CrO_3 = 2Cr_2O_3.CrO_3 + 3O.$$
(Violet or purple oxide)

$$(c) \qquad 4[2Cr_2O_3.CrO_3] = 10Cr_2O_3 + 3O_2.$$
(Green oxide)

The experiments so far made have not settled the point

Chemical Laboratory, 23, Holborn Viaduct, E.C.
March 23rd, 1907.

THE IGNITING POINT OF SULPHUR.*

By J. RUTHERFORD HILL, Ph.C.

At a meeting of the Pharmaceutical Society in 1890, I described an experiment indicating 248° C. as the igniting point of sulphur in air at ordinary atmospheric pressure (*Pharm. Journ.* xx., [3], p. 722). The apparatus employed is figured in Chemical News, lxi., p. 126.

Dr. W. R. Hodgkinson, of Woolwich, criticised this figure, and remarked that anything below 300 C. "is quite out of the question" (Chemical News, lxi. p. 96). His reason for this opinion is that a thin stream of boiling sulphur (temperature 448° C.) can be poured through air into water without ignition taking place, and this is assumed to be inconsistent with the statement that the igniting point in air is 248° C. Dr. Hodgkinson overlooks the fact, indicated in my paper, that he is pouring the liquid sulphur through an envelope or tube of vapour, much colder on the outside than the boiling sulphur, and which effectually prevents the free access of air shown to be necessary for ignition.

Mr. Bertram Blount repeated my experiment with a slightly modified apparatus, and found the igniting point 261° C., which he accepted in place of his previous determination of 270° C., on the ground that my method eliminated the previous sources of error (Chemical News, lxi., p. 153).

In December, 1903, there appeared in the *Pharmaceutical Journal* a brief abstract announcing that H. Moissan had determined the igniting point of sulphur in oxygen at ordinary atmospheric pressure to be 282° C., and in air 363° C.

This differed so widely from all previous determinations, that I wrote a letter to the Editor of the *Pharmaceutical Journal* affirming that the actual temperature of ignition was not lower than 248° C., and not higher than 261° C., and asking particulars of Moissan's method (*Pharm. Journ.*, [4], xvii., p. 939). There being no response to this letter, I communicated direct with H. Moissan in May, 1904, but received no reply. The recent decease of H. Moissan recalled the circumstance to my mind, and induced me to re-examine the subject. On looking up Moissan's original paper (*Comptes Rendus*, cxxxvii., p. 547) it is found that after several experiments he adopts the following method:—

"Some fused sulphur is kept in an atmosphere of CO_2 to prevent all formation of SO_2, and the oxygen is heated in the bath of liquid sulphur, in the middle of which the experiment is conducted. For this purpose we have placed 150 grms. of fused sulphur at the bottom of a flask of 250 cc. By means of a glass tube bent at a right angle, we conducted to the surface of the fused sulphur a sufficiently rapid current of dry CO_2. The oxygen was led in by a straight glass tube, whose end was completely submerged for a length of 5 to 6 cm. in the liquid sulphur, and was terminated by a narrow point.

"The oxygen was disengaged bubble by bubble much more slowly than in the previous experiments (which were at the rate of one litre in ten minutes). A thermometer indicated the temperature of the sulphur. Lastly, the flask was placed on a sand bath which was cautiously heated. Under these conditions, while the temperature is below 282° C., the oxygen disengaged bubble by bubble through the liquid sulphur produces SO_2, but without incandescence. On the other hand, when this temperature is reached, a more active reaction begins by a slight explosion, which is immediately followed by the phenomenon of incandescence. Beyond this temperature, the combination of oxygen and sulphur takes place with flame and with disengagement of heat, which rapidly increases and raises the temperature of the fused sulphur. The temperature of ignition of sulphur in oxygen under a

* Read before the Pharmaceutical Society of Great Britain, March 20, 1907.

pressure of one atmosphere is therefore 282° C. Under the same conditions, using air instead of oxygen, the temperature of ignition is 363° C. This combustion in the middle of a bath of fused sulphur has a blue flame, but being produced in a yellow liquid, it appears green. When the temperature is lowered to 360° C., the flame is no longer formed, and from this point, if the current of CO_2 is not very rapid at the surface of the sulphur, a series of explosions is produced, due to the mixture of air and sulphur vapour; that is to say, the temperature of ignition of this vapour of sulphur is lower than that of liquid sulphur, and is produced in air near 285° C.

"This temperature of ignition is rapidly raised when the air contains SO_2. In a mixture of 95 per cent of dry air and 5 per cent of SO_2 the igniting point is near 445° C. In 90 per cent of dry air and 10 per cent of SO_2, ignition does not take place at 465° C."

As Mr. Blount very properly remarks, the difference between his figure and mine may be due merely to difference in the actual dimensions and arrangement of apparatus and area of the surface of glass in contact with the mixed gases. The temperature of the ingoing current of air, and probably also the relative proportions of air and sulphur vapour, may make a difference of a few degrees, but a difference of 115° C. demands some other explanation.

I have repeated my experiment with apparatus of slightly larger dimensions, but otherwise identical with that figured in the CHEMICAL NEWS, except that, in addition to the thermometer in the sulphuric acid bath, there was a second thermometer inside the tube containing the sulphur. When both thermometers indicated 255° C., the sulphur vapour and air ignited, and continued to burn with a blue flame on the top of the sulphur in the bottom of the tube. Owing to a slight displacement of the aspirator, the thermometers had fallen to 246° C. before the air supply could be renewed, and at this temperature the vapour of sulphur refused to re-ignite. There was no time to repeat the experiment, but this is ample confirmation of the results obtained by me in 1890.

I have had some difficulty in following Moissan's process. He says that the igniting point in air at a pressure of one atmosphere is 363° C. But he conducts the air into the liquid sulphur through a tube which is immersed in the sulphur to a depth of 5 or 6 cm., or about 2½ inches. Liquid sulphur has a specific gravity of nearly 2, and therefore the pressure under which the air enters the sulphur, instead of being 760 mm. must be nearer 770 mm. I do not understand why he uses an atmosphere of CO_2 to wash out any SO_2. It would be as effectual and more suitable to use ordinary air, in sufficient quantity as I have done. Had he done so, it seems probable he would have got a very different result. He makes the statement that a mixture of sulphur vapour and air ignites about 285° C. From this, one might infer that he means to distinguish between the igniting point of sulphur in vapour and liquid sulphur. But is any such distinction possible? The igniting point of any volatile substance is surely the point at which its vapour inflames in air. Taking his own case, whenever a bubble of air enters the liquid sulphur it will be instantly saturated with sulphur vapour, and it is this mixture that becomes incandescent. More than that Moissan has shown that sulphur and oxygen combine to form SO_2 below the ignition point, consequently the confined portion of air in the bubble will at once become more or less contaminated with SO_2. He points out that a contamination with 5 per cent of SO_2 raises the igniting point to 445° C. May it not therefore be that his method, owing to the sources of error indicated and the abnormal conditions of the experiment, is altogether unreliable as an indication of the temperature at which sulphur ignites when freely exposed to the air at ordinary atmospheric pressure? My experience is that though some SO_2 may be formed, the quantity is very small, under the conditions of my experiment. I do not think it is the SO_2 which prevents ignition, but the formation of an envelope of vapour of sulphur, comparatively cold, which prevents the air getting access to the surface of the sulphur where the hot vapour is being given off. Moissan does not seem to take any account of this atmosphere of sulphur as an interfering agent, and I believe it to be the more important.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 158).

Confirmatory Experiments and References (continued).

Action of H_2SO_4 on Al_2O_3 and TiO_2.—Two grms. coarsely powdered corundum, which had been previously digested with HF, and 0·5 grm. rutile were in separate experiments boiled with 10 cc. H_2SO_4 (1·84) in a covered casserole for fifteen minutes; the mixture was diluted, filtered, and the filtrate made alkaline with NH_4OH; about 50 mgrms. Al and about half the titanium were precipitated as hydroxides.

100 mgrms. Al as Al_2O_3, obtained by igniting $Al(OH)_3$, were boiled with 5 cc. H_2SO_4 (1·84) in a covered casserole for ten minutes; a residue containing 10 to 20 mgrms. Al was left undissolved, and this did not dissolve completely on two more treatments with H_2SO_4. The experiment was repeated with 200 mgrms. Ti as ignited TiO_2; nearly all of it dissolved in three to four minutes.

P. 6, N. 1: *Action of Boiling Sodium Carbonate Solution on $BaSO_4$, $Cr_2(SO_4)_3$, and Sb_2O_5.*—500 mgrms. Ba as $BaSO_4$ were treated by the procedure; a residue of $BaSO_4$ corresponding to about 30 mgrms. Ba remained on adding HCl. This residue was treated a second time by the procedure; not more than 1 to 2 mgrms. Ba as $BaSO_4$ then remained.

100 and 200 mgrms. Cr as anhydrous $Cr_2(SO_4)_3$, obtained as described under C. E., P. 5, N. 4 and 5, were boiled with Na_2CO_3 in a covered casserole as described in P. 6; the pink precipitate slowly became greenish blue in colour. The Na_2CO_3 solution was acidified with HCl, and $BaCl_2$ added to it; a precipitate of $BaSO_4$ was formed, thus showing that chromic sulphate was being decomposed.

The greenish blue residue from the experiment with 100 mgrms. Cr (which in contrast to the anhydrous sulphate filtered easily) was boiled with HCl; some chromium dissolved, but the greater part was left as undecomposed anhydrous sulphate.

The greenish blue residue from the experiment with 200 mgrms. Cr was boiled for about two hours with seven successive portions of Na_2CO_3 solution, and these solutions were tested for sulphate. The sulphate in these portions steadily decreased in amount and the last portion was free from it. The greenish blue residue now dissolved completely in HCl on warming, and the solution gave no precipitate with $BaCl_2$, showing that the chromic sulphate had been completely converted into the hydroxide.

100 mgrms. Sb as antimonic hydroxide, obtained as described under C. E., P. 5, N. 4 and 5, were boiled with 25 cc. Na_2CO_3 solution in a covered casserole for fifteen minutes; the solution was acidified, and treated with H_2S; an orange precipitate of sulphide was obtained which was estimated to contain 3 to 4 mgrms. Sb.

*P. 6*a*, N. 1: *Precipitation of H_2WO_4 from Na_2CO_3 Solution by Acids.*—One mgrm. W as Na_2WO_4 was added in separate experiments to 5 cc. H_2O, to 5 cc. saturated Na_2CO_3 solution, and to 20 cc. Na_2CO_3 solution; HNO_3 was added in excess, and the solutions evaporated almost to dryness; yellow H_2WO_4 separated in the presence of HNO_3 alone, but not in the solutions containing $NaNO_3$. The latter were diluted with enough hot water

* From the *Technology Quarterly*, xix., No. 3 September, 1906.

to dissolve the salt, 1 to 2 cc. HNO_3 (1·20) were added, the solutions were boiled vigorously, and then cooled; yellow H_2WO_4 precipitated in the solution containing the smaller amount of salt, but not in the other solution:—The experiment with 20 cc. Na_2CO_3 solution was repeated except that 2 mgrms. and 3 mgrms. W (in separate experiments) were taken; no yellow precipitate was obtained with 2 mgrms., and only a slight one with 3 mgrms., thus showing that the presence of $NaNO_3$ interferes with the test.

Solutions containing, respectively, 1, 2, 5, 10, and 20 mgrms. W as Na_2WO_4 in 20 cc. Na_2CO_3 solution were evaporated with excess of H_2SO_4 to strong fuming, diluted to about 15 cc., boiled, and cooled again; no yellow precipitate was formed in any of the experiments:—Solutions containing 2, 3, 5, and 10 m.grms. W as Na_2WO_4 in 20 cc. Na_2CO_3 solution were evaporated with excess of HCl almost to dryness, diluted to about 15 cc., boiled, and cooled; no yellow precipitate was formed. The final solutions obtained in all these experiments turned blue when some granules of zinc were added, though the colour from 1 mgrm. W in H_2SO_4 appeared only after several minutes.

*P. 6*a*, N. 2: *Reduction of* H_2WO_4 *with Zinc*.—See v. d. Pfordten, *Ber.*, 1883, xvi., 508.

To 10 mgrms. W as Na_2WO_4 in a test-tube were added 5 cc. water, 5 cc. HCl (1·12), and a few granules of zinc; a white precipitate separated when HCl was added, and a deep blue colour resulted from the action of the zinc; after half-an-hour the blue colour had changed to a dark brown, and a dark coloured precipitate was suspended in the solution.

*P. 6*a*, N. 3: *Solubility of* H_2WO_4 *in Acids*.—Two mgrms. W as Na_2WO_4 were treated by P. 3, 4, and 5 except that no HF was added; a yellow precipitate of H_2WO_4 was obtained on boiling with HNO_3, and was not dissolved by dilute HNO_3 after the evaporation (P. 3); the residue dissolved in HCl (1·20) on boiling, but H_2WO_4 was re-precipitated on evaporating the aqua regia, and was not dissolved by the dilute HCl (P. 4). Nearly all the residue dissolved, however, in 2 cc. H_2SO_4 (1·84), and did not re-precipitate on diluting to 20 cc., and boiling (P. 5). (For the solubility of H_2WO_4 in concentrated H_2SO_4, and after dilution, see *Technology Quarterly*, 1904, xvii., 249).

P. 7. N. 2: *Effect of Fusing* Al_2O_3, SnO_2, TiO_2, MoS_2 *with* Na_2CO_3 *or with* Na_2CO_3 *and* KNO_3.—For the fact that a large residue remains when native Al_2O_3, TiO_2, and SnO_2 are fused with Na_2CO_3, see *Technology Quarterly*, 1903, xvi., 127.

80 mgrms. Al as Al_2O_3, obtained by igniting precipitated AlO_3H_3 over a blast-lamp for fifteen minutes, were fused with 8 grms. Na_2CO_3 in a platinum crucible over a powerful burner for twenty minutes; 0·2 grm. KNO_3 was then added, and the heating continued for ten minutes longer; the fusion was cooled, and digested with HCl; only a small residue of unattacked Al_2O_3, corresponding to 5 to 10 mgrms. Al, remained. The solution gave no precipitate with H_2S, showing that platinum had not been removed from the crucible.

500 mgrms. Mo as molybdenite (MoS_2) were fused for three to five minutes in a porcelain crucible with 10 grms. Na_2CO_3, and the mass treated with water; the black particles of MoS_2 all dissolved during the fusion, and the mass, which had a light red colour, dissolved nearly completely in water. HCl was added to the solution; a large black precipitate separated.

150 mgrms. Mo as molybdenite were fused for about two minutes in a platinum crucible with 8 grms. Na_2CO_3 and 0·5 grm. KNO_3, and the mass was treated with dilute HCl; complete solution resulted; the platinum crucible was not injured:—The experiment was repeated, except that the KNO_3 was added after a minute's fusion with Na_2CO_3; the result was the same.

P. 7, N. 2 and P. 8, N. 3: *Effect of Fusing* Al_2O_3, SnO_2, TiO_2 *with* KOH.—200 mgrms. of coarsely powdered corundum (Al_2O_3) that had been previously digested with HF and with concentrated H_2SO_4 and 200 mgrms. of finely powdered cassiterite (SnO_2) were fused with 10 grms. KOH in nickel crucibles for fifteen minutes; the mass was extracted with water, and the residue heated with HCl; a residue still remained, which was estimated to contain about half the Al_2O_3, but little, if any, of the SnO_2. An analysis was made of the aqueous extract and of the HCl solution; the former was found to contain about 50 mgrms. Al (as aluminate), and 100—150 mgrms. Sn (as stannate), but no nickel; the HCl solution contained 20 to 40 mgrms. Sn, 10 to 15 mgrms. Ni, and some Fe as chlorides, but no other metallic element.

One grm. of rutile containing 600 mgrms. Ti was treated by P. 3, 4, and 5; the residue was fused with KOH for about five minutes as described in P. 7, N. 3; the mass was extracted with water, and the residue treated with cold HCl (1·12); the rutile was not attacked by HNO_3 (P. 3) nor by HNO_3 and HCl (P. 4), but about 300 mgrms. Ti were dissolved by H_2SO_4 and HF (P. 5); much of the TiO_2 dissolved in the fused KOH, but only 2 to 3 mgrms. Ti passed into solution on treating the mass with water; out of the residue, which consisted of a black and white mixture, about 200 mgrms. Ti dissolved on treating with HCl (1·12); and a black residue of unattacked rutile still remained, which weighed 150 mgrms., corresponding to about 90 mgrms. Ti. This was powdered finely, again fused with KOH for fifteen minutes, and extracted with dilute HCl; all but 3 to 4 mgrms. Ti dissolved.

P. 8, N. 3: *Foreign Substances introduced from Porcelain or Nickel Crucibles*.—Ten grms. of a mixture of K_2CO_3 and Na_2CO_3 were fused in a porcelain crucible for half-an-hour over a powerful burner, the mass treated as described in the procedure, and the residue and solution analysed separately; the residue after the evaporation to dryness with HCl was shown by P. 5 to contain several mgrms. of SiO_2; the solution was found to contain several mgrms. of aluminium and of calcium, and a trace of iron. Compare also C. E., P. 8, N. 5 below.

The experiment was repeated, using a nickel crucible; the aqueous extract acidified with HCl gave no precipitate with H_2S, nor with NH_4OH and $(NH_4)_2S$. A slight black residue of nickel oxide insoluble in water remained; this dissolved in HCl, and gave a precipitate with NH_4OH and $(NH_4)_2S$, which was estimated to contain 1 mgrm. Ni. This experiment was repeated, except that 0·3 mgrm. KNO_3 was added to the fusion; 4 to 5 mgrms. Ni as nickel oxide were obtained.

Reduction of Silver and Lead Compounds by Fusion in a Nickel Crucible.—200 mgrms. Ag as precipitated AgCl were fused with 10 grms. of a mixture of Na_2CO_3 and K_2CO_3 in a nickel crucible for ten minutes, and the mass extracted with water; a residue of bright coloured metallic silver soluble in HNO_3 was left as a loose mass which did not adhere to the crucible, there being no evidence of the formation of an alloy.

200 mgrms. Pb as precipitated $PbSO_4$ were fused as in the preceding experiment; neither the aqueous extract (when acidified with HCl) nor the HCl solution of the residue gave precipitates with H_2S. The lead salt was completely reduced to metallic globules which had melted on to the nickel crucible, and were not dissolved off by fusion with KOH, KOH and KNO_3, KOH and Na_2O_2, or Na_2O_2 alone.

P. 8, N. 5: *Behaviour of Antimony and Tin Compounds on Fusion with Sodium Carbonate*.—60 mgrms. Sn as $SnCl_2$ and 50 mgrms. Sb as $SbCl_3$ were fused in a porcelain crucible with 10 grms. of a mixture of K_2CO_3 and Na_2CO_3 for half-an-hour; the fusion was extracted with water and with HCl as described in the procedure, and the solutions separately analysed; the aqueous extract contained nearly all the antimony and tin, a few mgrms. of silica, aluminium, and a little calcium; the HCl solution contained 4 to 5 mgrms. antimony, and 1 to 2 mgrms. each of aluminium, iron, and calcium.

(To be continued).

PROBLEMS OF APPLIED CHEMISTRY.*

By Prof. GEORGE LUNGE.

(Concluded from p. 162).

We, who have been born to see the ascendency of coal as the principal producer of energy in bulk, can hardly realise what a short epoch in the past and future history of mankind belongs to the age of coal. It has taken many thousands of years to form the beds of coal which exist in the earth's crust, and which have preserved to us a tiny portion of the solar energy radiated upon our planet during that period, millions of years ago. At that period, for various reasons, the production of living matter must have been incomparably more rapid than is the case at present. During untold ages this stored-up energy was lying idle, hidden under the accumulations of the more recent geological formations, not merely up to the advent of man, but through nearly the whole of his history. Leaving aside the tens of thousands or (according to some) hundreds of thousands of years during which man existed before the dawn of history, we must remember that historical documents exist in Egypt, Babylon, India, and elsewhere, taking us back at least 8000 years, and that the most glorious times of Greek and Roman civilisation are about 2000 years behind us. How modern, in view of these figures, is the use of the coal, and over what a short time it will extend! In these isles the use of coal is much older than in any other country, but even here its serious exploitation is comparatively recent, dating barely 150 years back; whilst its future (even if we disregard the more pessimistic estimates) is not likely to exceed some 200, or at most 300, years. Germany and the United States will probably hold out 200 or 300 years longer, but in all other countries the chances are all the other way.

Well, what is to happen then? Those countries where water power is abundant may possibly substitute electrical heating for that produced by the burning of coal, but what about England and Germany, which are so poorly off in that respect? Even in those countries which are more favoured the amount of water power is by no means infinite; and, if it had to be drawn upon, not merely for motive purposes, but for the production of electricity for heating purposes, it would be found insufficient in most places. Here we are faced by one of the greatest problems of applied science, both in chemistry and in physics, a problem which will give plenty of occupation to generations of future inventors. At present we can only surmise that some solution will present itself in the shape of a direct conversion of the sun's rays into other forms of energy; but the means by which this would be practically accomplished are at present quite uncertain.

The Age of Coal, in the midst of which we are living, short as it is evidently doomed to be in the long history of mankind, has been of incalculable service. For our purposes we may dismiss the earlier part of it, and look back only a hundred years. In all branches of industry, in locomotion, in the means of communication, and in innumerable matters ministering to the comforts of life, the progress since that time has been going on at a geometrical ratio. The present state of all these factors of civilisation in Europe (to say nothing of America) differs from that obtaining a hundred years ago far more than the latter differed from the Roman Era, or even from the age of the Egyptian kings. And this miracle has been brought about solely by *coal*, without the aid of which it is simply impossible to imagine the revolution which has taken place since then. "Railways!" That single word, to give only one instance, will bring this home to anyone who ponders over this matter. And it is equally impossible for us to imagine that, during the past century, there could have been any other invention, based upon the utilisation of the other supplies of energy of which we have spoken, which could have replaced the untold services of coal, that accumulator of solar energy, which alone has enabled the human mind to work out the thousand and one channels through which modern civilised life is flowing. We may say this with all confidence, for how otherwise could we account for the fact that such inventions have not been made in former times, when there were certainly quite as many ingenious minds in the world as during the coal-consuming age?

Let us now come down to considerations of a more modest, but more practical nature than those in which we have just been indulging. Seeing that the stock of mineral fuel upon this earth is so very limited, cannot we find means of husbanding it more than this has been done hitherto? It is only too notorious that the way in which coal is at present consumed is most wasteful. Of the energy residing in coal, most ordinary steam-engines utilise less than 10 per cent by converting it into mechanical motion; and even the most perfect steam-engines devised utilise hardly more than 15 per cent. Improvements in this direction may possibly swell this proportion a little, but there is no prospect of gaining much in that direction. Enormous wastages are also incurred in other ways. The conversion of pig-iron into steel, the manufacture of glass, and many other industries consumes from four to twenty times, and even more, of the quantity of coal required by theory. Many descriptions of coal are too poor to be used at all, except in the immediate vicinity of the spot where they occur; and in burning our fuel, whether it be for industrial or for technical purposes, we invariably send its nitrogen into the atmosphere, which surely contains quite enough of that commodity; the only exception being the manufacture of coal-gas, to which we shall refer later on. Here some of the grandest problems of applied chemistry present themselves to us—how to stop that fearful waste of fuel; and how to recover the nitrogen of the coal, if that be possible.

It is certain that we must look for the solution of these questions in the direction of converting coal into gaseous fuel. It is true that much has been done in that field in past years, and more especially will the name "Siemens" occur to every one in this connection, but much more remains to be accomplished. Another great stride ahead lies in the better utilisation of the waste gases from blast furnaces, in which respect the last few years have witnessed some very important improvements. All this refers merely to a better utilisation of the heating power of coal, but not to that other great task, the recovery of its nitrogen in a useful shape. This, together with the question how coal of poor quality is to be turned to a better account, has been tackled by the equally indefatigable and intelligently directed energy of Dr. Ludwig Mond, one of the benefactors of the Royal Institution. His invention, the "power-gas," has already attained a large measure of success, as is proved by the extent of the plants erected and designed. Mond's process belongs to that class by which we approach one of the greatest problems, for the time being, of applied chemistry; I mean the conversion of nitrogen from sources not yet opened out into ammonia and nitrates.

The immense importance of this latter problem lies in the fact that it touches our most urgent want, our supply of food. The soil of most countries, if tilled in the old manner, would not nearly suffice for the production of the requisite amount of food for men and cattle, while the limits of its producing capacity are being gradually narrowed down by exhaustion. Sir William Crookes, in his address to the British Association in 1898, has most forcibly drawn attention to this. The importation of food-stuffs from other less thickly populated countries can only modify, but not altogether extinguish, the danger of ultimate shortness of food at some future date, possibly not so very remote. It is certainly a great comfort to know that, with suitable manuring, the soil may be forced to yield even better crops than it would give in the virgin state, let alone in a condition impoverished by centuries

* A Discourse delivered at the Royal Institution, March 15, 1907.

of tilling. But stable manure is nothing like sufficient to attain that object, and we must turn to mineral fertilisers, principally phosphates, potassium salts, and nitrogen compounds. The two former classes of fertilisers are found in abundance in nature, and there is no danger apparently of their being exhausted during the next thousand years.

But the case is very different with the mineral forms of nitrogenous manures, *i.e.*, ammonium salts and nitrates. For agricultural purposes it does not make much difference whether we apply the nitrogen in one or the other of these forms. The ammonia, apart from insignificant quantities otherwise obtained, all comes from the nitrogen of the coal, but up to about twenty years ago only that coal which was used in the manufacture of gas was made to yield ammonia, and only one-sixth of its nitrogen was obtained in this form. In all other uses of coal, where at least twenty times as much is consumed as in the manufacture of gas, the nitrogen was simply sent into the air.

Quite recently, some progress has been made in the way of utilising some of this nitrogen as well. I have already mentioned the Mond process, where some of the nitrogen is recovered in the shape of ammonia: but this covers only one corner of the field. In another section a good deal has been already achieved. In the manufacture of coke, which is also a process of destructive distillation, and entirely analogous to gas making, very much larger quantities of coal are consumed than for the latter, since coke is indispensable for the smelting of iron and for other metallurgical purposes. Up to about twenty years ago all the volatile by-products in the manufacture of coke were lost—that is to say, tar, gas, and ammonia. The recovery of these by-products was first carried through in one or two French coke-works, about 1861, but nowhere else for a number of years, although in 1879 the late Dr. R. Angus Smith had earnestly recommended to the English coke-works the adoption of that system. Even now, both in France and England as well as in America, the recovery coke-ovens have found only a very limited adoption; in England perhaps 5 per cent of the coke is made in this way, against upwards of 50 per cent in Germany. In consequence of this, whilst twenty years ago Germany imported nearly all ammonium sulphate required for its agriculture from this country, she now imports none, and has, on the contrary, become a large exporter of that commodity. The reasons for this wonderful change are various. One of them is undoubtedly the revival of that spirit of push and enterprise which, after lying dormant for centuries in consequence of the ravages of the Thirty Years' War, caught up the German people, and enlivened German industry in all directions. Without going into details on this matter, we may take it that a considerable reserve of ammoniacal nitrogen exists in the quarter indicated, and that the present production of about half a million tons of ammonium sulphate might be greatly increased in that manner.

But that reserve, is, after all, nothing like sufficient to cover the requirements of agriculture in the future; and it is quite likely that in the long run all the really available nitrogen of the coal would not suffice for the wants of man. And what about the time when coal itself will be exhausted? Well, there is an eternal and inexhaustible source of nitrogen to which we must turn, and that is the atmospheric air. Four-fifths of this consists of nitrogen, calculated to amount to 4000 billions of tons, mixed with a quarter of that weight of oxygen. More than 100 years ago, in 1785, Cavendish discovered the fundamental fact that, by the action of the electric arc, the nitrogen of the air combines with oxygen to form nitric acid. The formation of ammonia from atmospheric nitrogen has also been effected, both by electricity and (which is more important) in other ways as well, as we shall see anon. But until a very few years ago these facts have never been put to any practical use, and the problem of turning the atmospheric nitrogen into ammonia, or nitric aid, although frequently approached in a purely scientific or, experimentally, in a technical way, had not been solved. Our days have seen the realisation of that most important task.

Let us first speak of ammonia. We are led up to this by what is, verily, a long and circuitous path. We must start from the discovery of calcium carbide (announced in 1862 by the celebrated Woehler), the technical preparation of which substance was first effected by Wilson in 1892, and about the same time by Moissan. True, the expectations that were entertained in various quarters in connection with this remarkable chemical product have not been fully realised to the extent anticipated by the inventors; but, on the other hand, an entirely novel use has been discovered for it by Professor Adolf Frank and Dr. Caro, of Berlin. They found that when nitrogen is passed over red-hot calcium carbide it is absorbed with formation of calcium cyanamide. This latter, when treated with water under high pressure, is made to yield ammonia; but it is not necessary to do this, since the crude product, which they have called "lime-nitrogen," can serve directly as nitrogenous fertiliser, and is in that respect equivalent to its own weight of ammonium sulphate. This is, indeed, its principal use for the present and the near future; but, as a matter of fact, the discoverers go much further. From the lime-nitrogen they prepare cyanogen derivatives of various kinds, some of which are valuable as constituents of explosives, and they are earnestly trying to employ it in the manufacture of nitric acid. They have also brought in several other industries—the manufacture of pure graphite, of pure hydrogen, of urea, and so forth. The pure nitrogen required for all this was at first produced by passing atmospheric air over red-hot copper; but it is now made by liquefying air and distilling off the oxygen, which is thus obtained as a valuable by-product. The inventors expressly recognise the invaluable aid which they have in this respect derived from the world-renowned researches of Sir James Dewar, carried out in the Royal Institution. The works already in operation, or in course of construction, will by the end of this year utilise water-power to the extent of some 55,000 horse-power, and will produce lime-nitrogen equivalent to 100,000 tons of nitrate of soda, and this with an expenditure of force less than one-third of that required for the process of Birkeland and Eyde, of which I shall speak directly.

I must, however, first say a word about the strenuous efforts made by Professor Frank and Dr. Caro, this time in connection with Dr. Ludwig Mond, to extract from *peat* both power and ammonia. Enormous, but hitherto almost worthless, deposits of peat exist in Ireland and North Germany; and the ultimate success of these endeavours, which we have every reason to hope for, will prove an incalculable boon to these countries. At the same time, all fears of a scarcity of ammonia for agricultural purposes would be thus removed for generations to come.

Important as ammonia is as a fertiliser, it ranks after the nitrates in that respect; and, unlike ammonia, the nitrogen of the nitrates is of immense importance for other purposes as well, viz., the manufacture of nitric acid and of explosives. The very limited quantities of nitrates required in former times, amounting to a few tens of thousands of tons per annum, were furnished by Indian saltpetre, that is, crude potassium nitrate. A far more abundant supply was opened out a little more than half a century ago, when the exploitation of the beds of nitrate of soda in South America was begun. The crude nitrate found there is refined on the spot, and comes to us as "Chilian saltpetre," which is almost pure sodium nitrate, to the tune of a million and a half tons per annum. About four-fifths of this is taken up by agriculture, the remainder serving, in the first place, for the preparation of nitric acid. As for that acid, it is impossible to imagine how we could do without it. Apart from minor, but quite indispensable uses, one of which is in the manufacture of sulphuric acid by the lead-chamber process, the greater part of nitric acid is consumed in the manufacture of coal-tar colours and in that of explosives.

Let us pause for a minute to consider the last-named. Even supposing it possible that all wars could be abolished on this terrestrial globe—a contingency not very likely to arise within the next few years, in spite of the laudable efforts of the Peace Societies—and that gunpowder were no longer required for shooting wild animals (an equally unlikely case, which would lead to a quite intolerable increase of game, big and otherwise)—we cannot conceive the possibility of our present system of civilisation enduring without a colossal consumption of explosives. How could we carry on mining operations without them? How could we get stones from the quarries? How could we construct roads, and tunnels, and railways without the help of explosives, all of which have a basis of salts or esters of nitric acid? And these have, up to the present, been prepared almost exclusively from Chilian saltpetre. The idea has certainly been mooted to imitate the natural process by which the nitrate is formed in India. This has been tried during a number of years in France and in Sweden, but has been given up as unprofitable in our northern climes. Also, the interesting experiment of sowing the bacillus of nitrification and of cultivating it in the soil has proved a failure, although I would fain believe that the last word has not been spoken on that subject. This, if successful, would replace some of the nitrate now used as fertiliser, just as a better utilisation of sewage would act in the same direction; but all this at the best goes only a very small way, and does not furnish the pure saltpetre required for the manufacture of nitric acid. What, then, shall we do when the nitre beds of Chili are exhausted? an event which, according to most estimates, is bound to take place within thirty or forty years from now. Unfortunately, there is no tangible hope of similar beds being found in any other localities, certainly not to any great extent. The beds of Atacama and Tarapaca on the Cordillera owe their origin to an altogether exceptional combination of climatic conditions and geological changes, the repetition of which in other quarters is exceedingly unlikely. Until very few years ago there was no prospect of any fresh supplies of nitrates in any other direction; but we may say that the solution of *this* problem, if not altogether settled in its final shape, has now been found. After many unsuccessful attempts at realising for practical purposes the discovery of Cavendish, and after a thorough investigation of its scientific principles by Lord Rayleigh, Muthmann and Hofer, Nernst, Haber, and others, this has been achieved, and once more, by means of that well-nigh omnipotent agent, electricity, which thus renders yet another service to mankind. At Notodden, in the Norwegian Hitterdal, a factory has been established to carry out the process of Birkeland and Eyde, who, by an ingenious application of the extreme heat produced by the electric current, make the nitrogen and oxygen of air combine to nitric oxide, which at a lower temperature is spontaneously oxidised into nitrous vapours, with the ultimate production of nitrites or nitrates. This time there is really no doubt that a practicable and economical process has been discovered for which it is intended to employ, by the end of this year, water power to the extent of 30,000 H.P. The Notodden process bids fair to be followed by other even more efficient processes. The most important of these is that of the Badische Anilin- and Soda-Fabrik, for which an experimental factory is in course of construction, and for which 50,000 H.P. are to be employed. But for some time to come the Chilian saltpetre will still rule the trade; a very large amount of water power will, indeed, have to be brought into use merely to cover the annual increment of consumption of this commodity for agricultural purposes.

One task it is certain that explosives will never fulfil, and that was suggested to me by one of the cleverest mechanical engineers I have known. He was intensely interested in the problem of aerial navigation, and for this purpose he wished to construct an engine worked by fuel of the most concentrated kind. Neither coal, nor benzine, nor oil would do. In his plight he came to me and asked what explosives I should advise him to try for working his engine, in the erroneous idea that explosives were a kind of concentrated fuel. Of course, I could not but reply as follows: All honour to his courage, but no explosive known, so far ever or likely to be invented, could possess that property he required, viz., a large store of energy. A pound of coal represents five time as much energy as a pound of the strongest explosive known—blasting gelatine. My friend had overlooked the fact that a pound of dynamite, though it gives out nearly 150 million horse-power, does so only for the space of 1/50,000 of a second. He had omitted to take into account the element of *time* and had confused *power* in the ordinary sense with *energy*, which is the capacity for doing work.

A similar confusion is sometimes made between energy and the creation of high temperatures. This can be very well illustrated by the use recently made of finely-powdered aluminium, both as a component of explosives and as an agent for producing very high temperatures, in the shape of Dr. Goldschmidt's "thermite." In both cases the fact is utilised that aluminium is easily, and in the shape of fine powder, almost instantaneously, converted into its oxide, alumina, by substances capable of giving off oxygen. In the case of thermite, a mixture of finely-powdered aluminium and ferric oxide is, when lighted, decomposed instantaneously into molten iron and aluminium oxide. The heat produced thereby far exceeds that produced by coal in any conceivable way; it is equal to that of the electric arc. One of the most important applications of this agent occurs in the welding of the ends of railway rails, when already laid down, into one continuous rail of any length required. And yet the total energy of thermite is only 450 thermal units per kilogram, or in other words, about one-twentieth of that of the best coal. But, whereas it takes a good deal of time to burn a pound of coal, during which process there is a great loss of heat by radiation, and the heat is spread over a current of gases which we call the flame, a pound of thermite burns off in about one second, and, as there are no gaseous products formed, all the heat generated remains within the molten iron and the alumina, which accounts for the extreme degree of heat to which these are brought.

Electricity has often been invoked to produce the most important of all inorganic products, iron. If this problem could ever be solved in an economical way, it would bring about a perfect revolution in the position of the leading nations. On the one hand, the enormous quantity of coal now consumed in the production of iron and steel (which is probably at least a quarter of the entire output of coal) would be set free for other uses, and the exhaustion of the coal-fields would be put off to a corresponding extent. On the other hand, the production of iron would pass over into the hands of those nations which command the largest amount of water-power, and which, therefore, can produce electricity most cheaply. Of the three countries which now produce between them the bulk, that is seven-eighths, of the world's iron, Great Britain and Germany would go to the wall, and the United States, which already produce more iron than these two countries put together, would become omnipotent in that field. Sweden, Italy, and some other countries would, at any rate, greatly increase their present production. But this radical change is, as yet, far off. No proof has, so far, been given that pig-iron, or the ordinary descriptions of wrought-iron and steel, can be generally produced by electricity at anything like the price at which it is now done by coal in the great industrial centres. Where a certain success has been scored in the electrical metallurgy of iron, it is for the refining of ordinary iron into a superior grade of steel which fetches an extraordinarily high price, and in the production of certain alloys of iron with chromium, nickel, and the like, whereby so-called special steels are obtained. But if at the present moment we do not see our blast furnaces and Bessemer works threatened by the competition of electrical iron, who can tell how soon this may not be the case?

The limits of my time have been too nearly reached for me to discourse upon many other problems which present themselves in inorganic applied chemistry, and only a few minutes are left to speak of those belonging to the domain of organic chemistry.

I will point to only two problems of this kind. One of these is the substitution of artificial for natural colouring matters. This, indeed, has now been carried out almost to the bitter end. Long ago, one of the oldest and most widely-used colouring matters, that contained in madder, succumbed to the attacks of the chemists, among whom the names of Edward Schunck and William Henry Perkin testify to the glorious share taken by Englishmen in that victory. The colouring substance of madder—alizarine—is now made from English coal-tar, and has altogether taken the place of the impure form in which it occurs in the madder plant. The growers of this plant in the south of France and elsewhere have had to abandon its culture altogether, to their great sorrow.

A similar fate has already partly overtaken, and may, in the end, destroy entirely, the culture of indigo, most of which, as you know, comes from British India, and formerly represented a value of some four million pounds sterling per annum. At first, after the great Munich chemist, Adolf Baeyer, had prepared the colouring matter of indigo by synthesis in his laboratory, the planters merely shrugged their shoulders, and that with good reason, since Baeyer's processes could not compete with their produce in respect of cost price. Another circumstance which at that time militated against artificial indigo was this, that it started from toluene, the total available quantity of which substance would not have sufficed for producing anything like all the indigo required, even if no toluene were used for other purposes, which is out of the question. But this state of matters has changed. Twelve years ago the late Carl Heumann, assistant professor in my laboratory at Zurich, discovered the synthesis of indigotine from naphthalene. This, like toluene, we get from coal-tar, but in about ten times the quantity, so that there is no fear of any scarcity of naphthalene even in the future. The late Dr. Rudolph Knietsch at the Badische Anilin und Sodafabrik at Ludwigshafen gradually transformed Heumann's laboratory process into a factory process, which is working with entire success on a large scale. Synthetic indigotine is now manufactured at such a low price that its competition has proved a severe blow to the indigo-planting interests. Thus the triumph of scientific investigation and practical skill in chemical manufacturing, gratifying though it be as a splendid achievement of applied chemistry, is a sad trial to many thousands of Indian ryots and their British masters; and this is merely the foretaste of what will inevitably happen in many other cases. What is food for one is poison for another. But yesterday this was the bitter experience of the French madder-grower; to-day it is the turn of the Indian indigo-planter; and to-morrow it may be some one else's lot.

Most other vegetable colouring-matters, several of which have also been synthetically produced, have become useless by the discovery of hundreds, and even thousands, of artificial colouring matters far exceeding them in beauty, and often also in fastness. On this well-known point I cannot dwell now.

In conclusion, I would touch upon what is, perhaps, the very greatest problem of applied chemistry, and that is the direct production of feeding-stuffs for man and beast. The synthesis of alimentary substances from inorganic matter has, up to this moment, not been even remotely achieved, nor can we at present so much as guess the direction in which this might be done; whilst, as for the production of food from sawdust and other waste organic substances, we are in no better case. But even here the word "impossible" should not be pronounced. In a more modest form, at all events, chemistry has found magnificent scope in that quarter—I mean in the extraction of alimentary substances from new sources and in the increase of production from old ones. The colossal industry of beet-root sugar is an instance of the former, whilst agricultural chemistry, as a whole, works in the latter direction.

But this is really too vast a subject to be discussed at the fag-end of this lecture, and I must, therefore, content myself with the foregoing few remarks, and beg to take leave of my esteemed audience.

FOOD ADULTERATION.*

Report of Committee C.—H. C. Lythgoe, *Chairman*.

I. Colours.

It is recommended—

1. That, as suggested by the Associate Referee for 1905, the co-operative work on colours be continued along the following lines:—

a. Solubility of the coal-tar and vegetable dyes in various solvents (ether, acetic ether, petroleum ether, methyl and ethyl alcohols, acetone, &c., and mixtures thereof), arranged according to their solubility—as easily soluble, difficultly soluble, and insoluble,

b. Extractive values of the various solvents for dyes in neutral, acid, and alkaline solutions.

c. Characteristics of the colouring matters as contained in fresh fruits, vegetables, wines, &c., with reagents and solvents, including their respective dyeing properties.

Adopted.

2. It is the sense of the committee that the term "vegetable colours" is a misnomer as applied to the products studied by Mr. Nickles, and the committee recommends that this portion of the report be returned to the Referee with the suggestion that the words "commercial colours alleged to be vegetable colours" be substituted for the words "vegetable colours" and that this portion of the report be revised accordingly.

Adopted.

2. Saccharine Products.

The Referee made no formal recommendations, but suggested that if the work on maple products was continued the three methods tried for the determination of the lead number be given a thorough trial, and that the work on the malic acid value be continued until a modification is secured which gives more uniform results in the hands of different chemists. (Method 1—Winton, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1204. Method 2—Sy, *Journ. Franklin Inst.*, July, 1906, p. 71. Method 3—Hill and Mosher, *Technology Quarterly*, June, 1905, xviii., [2], 147).

No action was taken by the committee on these suggestions, which are submitted for the information of the Referee for 1907.

3. Distilled Liquors.

It is recommended that a further study be made of the determination of fusel oil.

No action taken by committee and recommendation goes to the Referee for consideration.

4. Beer.

The following recommendation was not acted upon by the committee, as it involves action as to an official method, and is referred to the Referee for 1907 for recommendation as to final action, together with the suggestion made as to the revision of the alcoholometric tables:—

I suggest that a committee be appointed by this Association for the purpose of revising the alcoholometric tables now given in *Bulletin* No. 65, that they may be adopted for use at this new temperature (20° C.). I furthermore recommend the adoption of the following methods of beer

* Extracts from the Proceedings of the American Association of Official Agricultural Chemists, 1906.

analysis as official for this Association. (See *Circular* No. 33, Bureau of Chemistry, for detailed statement of methods).

5. Infants' and Invalids' Foods.

It is recommended that the subject "Infants' and Invalids' Foods" be dropped.

Adopted.

6. Condiments other than Spices.

It is recommended that the methods outlined by the Referee be adopted provisionally, but that in printing the same they be given by reference wherever such methods appear under other subjects.

Action deferred for one year.

7. Tea and Coffee.

It is recommended—

1. That the methods outlined by the Referee for the estimation of caffetannic acid be submitted for co-operative study by the members of the Association.

These methods are as follows:—

Bell's or Payen's method, "Chemistry of Foods," vol. i., p. 48; Proctor's modification of Lowenthal's method, Chemistry *Bulletin* No. 13, pt. 7, p. 890; Krug's method, *Ibid.*, p. 908; Trillich and Guckel's method, *Zeit. Nahr. Genussm.*, 1898, p. 101; hydrolytic method, Howard: Boil 5 grms. of coffee one-half hour with 100 cc. of water, and decant the extract through a filter. Repeat this treatment several times and make the filtrate up to 500 cc. Precipitate 200 to 400 cc., equivalent to 2 to 4 grms. of coffee, with lead acetate, wash the precipitate sufficiently to remove the small proportion of sugars present, and submit to hydrolysis by heating in a water-bath with hydrochloric acid. Estimate the reduction sugars by Allihn's method, and calculate to caffetannic acid for both the mono- and di-glucoside formulæ, considering the reducing sugars as $C_6H_{12}O_6$.

Adopted.

2. That the Gomberg method for the determination of caffein be subjected to trial. This method can be logically carried out in connection with the caffetannic acid estimation, and is essentially as follows:—

The filtered extract, prepared by boiling the material with water, is precipitated by lead acetate, and the precipitate filtered off and thoroughly washed with water. The excess of lead is removed from the filtrate by sulphuretted hydrogen, and the latter expelled by boiling. An excess of a standard solution of iodine in potassium iodide is added, the precipitate of the alkaloid with iodine filtered out and the remaining iodine estimated by titration with sodium thiosulphate.

Adopted.

8. Food Preservatives.

It is recommended that the following changes in *Bulletin* No. 65 be made:—

1. Page 109—The second method for the detection of benzoic acid to be re-written as follows:—

Evaporate to dryness and treat the residue with 2 or 3 cc. of concentrated sulphuric acid. Heat until white fumes appear. This chars the organic matter and converts the benzoic acid into sulphobenzoic acid. Add a few crystals of ammonium or potassium nitrate and again heat the dish until white fumes appear. Repeat this process until all organic matter is oxidised and the solution is practically colourless. This causes the formation of metadinitrobenzoic acid. When cool, dilute with an equal volume of water, add ammonia in excess, and transfer the solution to a test tube. Cool and add a few drops of freshly-prepared ammonium sulphide in such a way that the solutions do not mix. The nitro compound is thus converted into ammonium metadinitrobenzoate, which possesses a red colour. This reaction takes place immediately, and is seen at the surface of the liquid without stirring.

2. Page 90, line 2—Substitute "20 cc." for "5 cc." This change is considered advisable, because, when determining sulphurous acid in meat products, about 20 cc. of 20 per cent phosphoric acid is found to be necessary to completely evolve the sulphurous acid present. This amount would not be required for wines, but as there seems to be no objection to the use of the excess of phosphoric acid in this case, it is thought advisable to recommend a uniform quantity of phosphoric acid, which will answer for all purposes.

3. Page 90, after line 34, insert—

Instead of titrating the excess of iodine with the standardised thiosulphate solution, the sulphurous acid distilled over may be determined directly by acidifying the iodine solution, or an aliquot thereof, with hydrochloric acid, boiling until colourless, and precipitating sulphuric acid in the usual way with barium chloride.

4. Page 110, line 41—Transpose the phrase "boiled to expel carbon dioxide," to line 40, inserting the same after the word "pink."

5. Page 110—Under method for boric acid insert the following method:—

Weigh about 50 grms., make alkaline with milk of lime, evaporate to dryness, and ignite as directed under the determination of ash in general methods. Dissolve in hydrochloric acid, filter, and wash. In case much carbon remains, burn the paper and residue after making alkaline with milk of lime, and treat with hydrochloric acid as above. Make the filtrates alkaline with sodium hydroxide, boil, add barium hydroxide until no further precipitate is formed, and filter. Dissolve the precipitate in dilute hydrochloric acid, and re-precipitate with sodium hydroxide, with the addition of a few drops of barium hydroxide. Wash the precipitate with hot water, cool the filtrate and washings to room temperature, and dilute to definite volume. Take an aliquot portion, add methyl-orange, and acidify. Boil to expel carbon dioxide, cool, and add decinormal alkali until the pink colour is just discharged. Add 5 or 6 grms. of mannite and a few drops of phenolphthalein, and titrate the boric acid, which is now all in the free state, with decinormal alkali. When the end point is obtained, it is well to add more mannite, to be sure that enough has been used. Owing to the solubility of barium phosphate, the results obtained by this method should be corrected by a blank determination in which a food free from boric acid is employed. In all cases the operation should be conducted uniformly with respect to volume of solution in which the precipitations are made, and amount of washing.

6. Eliminate from methods for salicylic acid directions to extract the residue with gasolin.

7. Page 73—Eliminate the resorcin method for formaldehyde, inasmuch as this method is unreliable, and there are better methods available.

Action deferred for one year.

It is further recommended that the referee for the ensuing year conduct work along the following lines:—

(1). Quantitative determination of salicylic acid in wines.

(2). Further experiment for the determination of salicylic acid in fruit products, such as jams, marmalades, &c.

(3). Further trial of Harty and Mummery's method (*Analyst*, 1905, xxx., 124).

(4). Trial of method for the detection and determination of fluorides proposed by Woodman and Talbot (*Journ. Am. Chem. Soc.*, xxviii., 1437).

9. Determinanion of Water in Foods.

It is recommended that the study of the vacuum method for the determination of water be continued next year, and that the methods employed for study shall be:—(*a*) The present vacuum method in either the Hempel or Scheibler type of desiccator; (*b*) the vacuum method with any modification which may facilitate drying, as the introduction of phosphorus pentoxide as a drying agent; (*c*) drying in partial vacuum in a current of dry pre-heated air and inert gases.

Adopted.

10. General Recommendations.

The Committee recommends that the Associate Referees on the following subjects study the determination of alkalinity of soluble and insoluble ash with a view to obtaining uniform results: — Saccharine products, including confectionery; fruit products, wine, beer, vinegar, spices, dairy products (in reference to calcium sucrate in cream), cereal products, vegetables, cocoa and cocoa products, tea and coffee.

Adopted.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1907.

Sir Henry E. Roscoe, F.R.S., Past President, in the Chair.

(Concluded from p. 164).

66. "*Some Compounds of Guanidine with Sugars.*" (Part I.). By Robert Selby Morrell and Albert Ernest Bellars.

When an alcoholic solution of guanidine is added to dextrose, lævulose, mannose, arabinose, rhamnose, galactose, or maltose, dissolved in ethyl alcohol, white microcrystalline precipitates are obtained. The general formula for dextrose-, lævulose-, and mannose-guanidine is $3C_6H_{12}O_6.2CN_3H_5$. In N/2 solutions, the compounds are dissociated into their components to the extent of 71 per cent. The depression of the freezing-points of mixed dextrose and guanidine solutions was determined on the lines of H. Euler's researches (*Ber.*, 1905, xxxviii., 2551; 1906, xxxix., 350), and the results confirm his view as to the acid character of carbohydrates in aqueous solution. The strength of guanidine as a base compared with caustic soda was determined by (*a*) the saponification of ethyl acetate, (*b*) the velocity of fall in rotation angle of a hyoscyamine solution in the presence of guanidine (Will and Bredig, *Ber.*, 1888, xxi., 2777). The strengths of guanidine and caustic soda were found to be in the ratio of 0·8 : 1. Aqueous solutions of dextrose-, lævulose-, or mannose-guanidine show a gradual fall in optical rotation to a minimum value, which is the same for the three compounds. This behaviour is similar to that investigated by Lobry de Bruyn in the action of alkalis on sugars. The results obtained from the study of the mutarotation of solutions of dextrose-, lævulose-, or mannose-guanidine may be summarised as follows:—1. The fall in optical rotation to a constant minimum represents an apparent equilibrium in the case of dextrose- and lævulose-guanidine between two sugars through an intermediate substance, X, the concentration of which is very small, G $\rightleftharpoons$ X $\rightleftharpoons$ F. 2. The velocity constants for the transformation of dextrose into lævulose, and *vice versâ*, were found to be 0·0015 and 0·0021 respectively; the velocity constants for the change of mannose into lævulose and dextrose are 0·0005 and 0·00036 respectively. The velocity of the reverse change of lævulose and dextrose into mannose is very small. 3. There is a slow disappearance of X, the intermediate substance, to form acids. When optical equilibrium has been reached, the ratio of lævulose to dextrose remains constant until the formation of acids ceases. The changes may be represented by the scheme—

67. "*The Action of Aluminium Chloride on Naphthalene. Formation of ββ-Dinaphthyl, Tetranaphthyl, and Tetramethylerythrene.*" By Annie Homer.

The action of aluminium chloride on naphthalene has been studied in detail. *ββ*-Dinaphthyl, $C_{20}H_{14}$, was formed, as had been indicated by Friedel and Crafts. Besides this compound, three new hydrocarbons were isolated, namely:—(1) An oil, $C_{14}H_{16}$, probably *tetramethylnaphthalene*; (2) a resinous hydrocarbon, $C_{26}H_{22}$, to which the name *tetramethylerythrene* has been given; and (3) a yellowish red solid, *tetranaphthyl*, $C_{40}H_{26}$.

Tetramethylerythrene is deep red, and its solutions, besides being highly fluorescent, show two absorption bands in the blue and violet portions of the spectrum respectively.

ββ-Dinaphthyl and tetranaphthyl are produced by condensation of the naphthalene molecules. The mode of formation of tetramethylerythrene is open to question.

68. "*Mercurous Hyponitrite.*" By Prafulla Chandra Ray.

The author has succeeded in preparing this salt in a purer form than that described in a former paper (*Trans.*, 1897, lxxi., 348). A solution of mercurous hyponitrite in nitric acid, unlike the silver salt, undergoes slow dissociation into mercury and mercuric hyponitrite.

69. "*The Decomposition of Mercurous and Silver Hyponitrites by Heat.*" By Prafulla Chandra Ray and Atul Chandra Ganguli.

The gaseous products of decomposition of mercurous hyponitrites are nitrogen, nitrogen monoxide, and nitrogen dioxide, the proportion of the first being very small.

Silver hyponitrite also yields the same gases with a much larger proportion of nitrogen dioxide. The authors are of opinion that these salts have both an oxylic and imidic constitution.

70. "*Studies in Optical Superposition.*" (Part III.). By Thomas Stewart Patterson and John Kaye.

l-Menthyl diacetyl-*i*-tartrate has been prepared and its rotation has been determined both in the homogeneous state and in solution in ethyl alcohol, benzene, and nitrobenzene. The results, taken in conjunction with those previously published (*Trans.*, 1905, lxxxvii., 33; 1906, lxxxix., 1884), furnish for the first time thoroughly valid evidence as to the untenability of van't Hoff's assumption regarding optical superposition.

The accompanying table exhibits this comparison at different temperatures for the homogeneous substances, and also gives the values found for solutions (see next page).

Both in the homogeneous condition and in solution therefore the rotation of the *i*-tartrate is markedly greater (that is, less negative) than the means of the values for the *d*- and *l*-tartrates, and this furnishes conclusive evidence that the rotation due to a given asymmetric atom in a compound of two or more asymmetric radicles is not independent of the configuration of the other group or groups with which it is combined.

71. "*An Extension of the Benzoin Synthesis.*" By Reginald William Lane Clarke and Arthur Lapworth.

Although mandelonitrile or its benzoyl derivative is too unstable to condense with *αβ*-unsaturated ketones, yet its aniline derivative, benzylideneaniline hydrocyanide, can be made to do so,

With carvone, *phenylimino-β-benzoyldihydrocarvone* is obtained:—

$$\begin{matrix}NHPh\\CN\end{matrix}\!\!>\!CHPh + CH\!\!<\!\!\begin{matrix}CMe{\cdots}\\C_6H_{10}\end{matrix}\!\!>\!CO =$$

$$= NPh{:}CPh{\cdot}CH\!\!<\!\!\begin{matrix}CHMe\\C_6H_{10}\end{matrix}\!\!>\!CO + HCN,$$

and this, on hydrolysis with acids, yields two stereoisomeric *β-benzoyldihydrocarvones*.

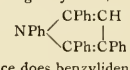
With benzylideneacetophenone, *γ-cyano-α-benzoyl-γ-anilino-βγ-diphenylpropane* is the product:—

$$\begin{matrix}NHPh\\CN\end{matrix}\!\!>\!CHPh + CHPh{:}CH{\cdot}CO{\cdot}Ph =$$

$$= \begin{matrix}NHPh\\CN\end{matrix}\!\!>\!CPh{\cdot}CHPh{\cdot}CH_2{\cdot}CO{\cdot}Ph,$$

		I. *l*-Menthyl diacetyl-*a* tartrate.	II. *l*-Menthyl diacetyl-*l*-tartrate.	III. Mean of I. and II.	IV. *l*-Menthyl diacetyl-*i*-tartrate.	Δ. IV.—III.
			Homogeneous Substances.			
t°	20°	−256°	−360°	−308°	−274°	34°
	100°	228	382	305	280	25
	130°	216	390	303	282	21
			Solutions.			
Solvent	Ethyl alcohol ..	−268° (*p* : 5)	−367° (*p* : 5)	−317·5	−292° (*p* : 0·455)	25·5°
	Benzene	285 ,,	313 ,,	299·0	248 (*p* : 5·2)	51·0
	Nitrobenzene ..	238 ,,	355 ,,	296·5	244 (*p* : 4·38)	52·5

the constitution of which was shown by converting it by heat into water, hydrogen cyanide, and tetraphenylpyrrole,



In neither instance does benzylideneaniline alone afford any analogous products. These condensations were shown to be extensions of the well known "benzoin synthesis" as interpreted by one of the authors (*Trans.*, 1903, lxxxiii., 1004).

72. "*Interaction of Starch and Carbon Disulphide. Xanthogenic Esters of Starch.*" By CHARLES FREDERICK CROSS, EDWARD JOHN BEVAN, and JOHN FREDERICK BRIGGS.

Alkali starch in its hydrated forms is a gelatinous impenetrable mass which is only superficially attacked by carbon disulphide.

Starch moistened with the disulphide and then treated with a sodium hydroxide solution (15 to 20 per cent) is brought into the condition for quantitative reaction and conversion into the xanthogenic ester (sodium salt). The derivatives are analogous in all respects to those of cellulose (*Trans.*, 1893, lxiii., 837).

73. "*The Estimation of Small Quantities of Nitrogen Peroxide.*" By ROBERT ROBERTSON and SIDNEY SCRIVENER NAPPER.

The method depends on the changes observed in the characteristic absorption spectrum of nitrogen peroxide as its concentration in dilute mixtures is increased. It was found that a few of the more prominent groups of lines were visible at a concentration of 0·05 per cent nitrogen peroxide, and that as the proportion was raised the lines increased in intensity and number until the violet end of the spectrum was completely absorbed in mixtures approaching a concentration of 1·0 per cent. These differences are sufficiently well marked to enable a process to be worked out for the quantitative estimation of the concentration by comparison with standard mixtures. Photographic comparison was employed, and for this purpose a series of standard photographs covering a range of concentration from 0·05 to 1 per cent was prepared.

The method when applied to the estimation of small quantities of nitrogen peroxide in air gives very satisfactory results, and the process which is applicable to any gaseous mixture has been used successfully for the investigation of the gases evolved during the slow decomposition of gun-cotton.

74. "*The Evolution of Nitrogen Peroxide in the Decomposition of Gun-cotton.*" By ROBERT ROBERTSON and SIDNEY SCRIVENER NAPPER.

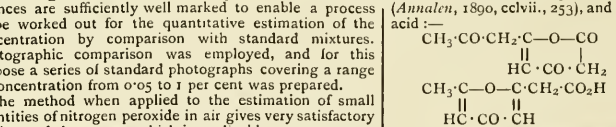
Previous investigators have given accounts of experiments in which gun-cotton was slowly decomposed at temperatures near 130° in a vacuum and in a current of carbon dioxide, and have stated that only a small quantity of nitrogen peroxide was evolved, or have made no reference to its presence. With the help of the method described by the authors (compare preceding paper) a careful study has been made of the gases given off by gun-cotton when heated under various conditions.

These include heating (1) in a vacuum; (2) in a stream of carbon dioxide; (3) in an unchanged atmosphere of carbon dioxide; (4) in nitrogen dioxide; and (5) in air. In all cases more than 10 per cent of the total nitrogen evolved was in the form of nitrogen peroxide, and a study of the results shows that the proportion is largely dependent on the conditions of experiment; the deposition of water and prolonged contact with the heated gun-cotton tend to reduce it, and when these two conditions are not present the proportion rises to 40—50 per cent. This occurs when the gun-cotton is heated under the conditions of the Will test, and reduction of the rate of the current of carbon dioxide causes a reduction of the proportion of nitrogen peroxide evolved. This effect is apparently due to the action of the nitrogen peroxide on the gun-cotton, and is accompanied by a rise in the total amount of nitrogen evolved, indicating that oxides of nitrogen cause an increase in the rate of decomposition of gun-cotton.

75. "*An Isomeric Change of Dehydracetic Acid.*" By JOHN NORMAN COLLIE and THOMAS PERCY HILDITCH.

During the preparation of a large quantity of triacetic lactone, it has been noticed that if sulphuric acid of about 85 per cent instead of about 90 per cent is allowed to act on dehydracetic acid, the yield of triacetic lactone is much diminished. On pouring the product into water, an acid, $C_8H_8O_4$, isomeric with dehydracetic acid, has been separated. It has a molecular weight of 169, is a true acid, not a lactone, melts at 99°, and has an electrical conductivity $k = 0{\cdot}00152$. When heated to about 200° it is converted almost quantitatively into carbon dioxide and dimethylpyrone. On boiling with excess of strong solution of barium hydroxide it yields barium acetate, acetone, and barium malonate. A solution of the neutral sodium salt on boiling is converted into sodium dehydracetate, from which dehydracetic acid is precipitated by adding an acid.

The free acid, when heated with an excess of ammonia, gives the ammonium salt of a lutidonecarboxylic acid. This acid, $C_8H_8O_4$, seems to agree in all respects, except its electrical conductivity, with an acid obtained by Feist (*Annalen*, 1890, cclvii., 253), and is a true pyronecarboxylic acid :—



Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 8th inst.; Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Mr. E. T. Hanson, Mrs. H. Loeffler, Sir Alexander Pedler, C.I.E., Dr. J. Percy Smith, Mr. F. H. Sully, Mr. A. H. Tubby, F.R.C.S., and Mr. C. A. Woods were elected Members. The Special Thanks of the Members were returned to Sir Andrew Noble, Bart., K.C.B., for his donation of £200 to the Fund for the Promotion of Experimental Research at Low Temperatures; and to Lady Kelvin for her Gift of a Statuette of the Rt. Hon. Lord Kelvin, G.C.V.O. The Chairman announced the decease of Professor M. Berthelot, Hon.Mem.R.I., and of Dr. Allen Macfadyen, Fullerian Professor of Physiology in the Royal Institution 1901-3, and Resolutions of condolence with the relatives were passed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 3, 1907.

Isomeric Cinnamic Acids.—E. Erlenmeyer, jun., C. Barkow, and O. Herz.—The authors have subjected the isomeric cinnamic acids to a crystallographic examination, and find that the different modifications can be distinguished from one another by their forms, and also that they have different melting-points and different solubilities. The acids are—(I.) Erlenmeyer's (sen.) isocinnamic acid, melting-point 37—38°; (II.) Liebermann's allocinnamic acid, melting-point 68°; (III.) Liebermann's isocinnamic acid, melting-point 59°; (IV.) α-cinnamic acid, melting-point 134—135°; (V.) β-cinnamic acid, melting-point 132—133°; (VI.) Erlenmeyer's (jun.) isocinnamic acid, melting-point 59°. Storax cinnamic acid and synthetic cinnamic acid differ in crystalline form and in solubility. The author's experiments with brucin show that the allocinnamic acid disappears when a salt is formed, and two salts of the same composition, but different properties and different rotatory powers, result. From them the Acids III. and VI. can be isolated, but under certain conditions transpositions of the salts are very probable, and when the acids are set free transpositions likewise may occur.

Preparation of Optically Active Butyl Alcohol.—R. Meth.—A convenient and rapid method of splitting racemic alcohols into their active components is the following:—Butyl alcohol is mixed gradually with three-fifths of its volume of concentrated sulphuric acid, meanwhile cooling; the mixture is allowed to stand for a day at the temperature of the room, and then poured into a suspension of barium carbonate in water. The filtrate is evaporated, which causes some decomposition, and finally, after repeated filtration, evaporated over sulphuric acid. The yield of crystalline barium butyl sulphate amounts to 18 or 19 grms. from 20 cc. of alcohol, thus roughly 35 per cent. The salt is exceedingly soluble in water, but can be re-crystallised from a little hot water. The barium salt is dissolved in water, the calculated quantity of brucin sulphate is added, the solution is filtered from barium sulphate and evaporated. After standing over-night the salt of the dextro-acid separates out as crystals, and can be purified by re-crystallisation from acetone or a little hot water. It melts at 210°, undergoing decomposition. The brucin salt of the lævo-acid also crystallises, but the separation of the two salts does not present the least difficulty. The brucin salt was again converted into barium salt and its rotatory power determined in aqueous solution, and compared with the rotatory power of the crystals first obtained by the evaporation of this solution. The two values agreed within the limits of errors of observation, and thus the separation of the brucin salts was complete.

Abnormally Coloured Complex Metallic Salts of Acid Imides.—H. Ley and F. Werner.—The authors' experiments provide a striking illustration of the fact that when side valencies are called into action the characteristic light absorption of a coloured salt is often totally changed. Thus copper succinimide, $Cu(NC_4O_2H_4)_2.6H_2O$, is blue, but the complex salts, $Me_2Cu(NR)_4$ (where Me = alkali metal and HNR = acid imide), prepared by the action of copper acetate on the alkali salts of the acid imide, are red or violet-red. Copper succinimide, $Cu<^{NR}_{NR}$, contains a metallic nitrogen bond, which causes no abnormal absorption of light; if, however, the other valencies of the metal are called into action, as in $^{NH_3}_{NH_3}>Cu<^{NR}_{NR}$, such abnormal absorption occurs, and the compounds become red or reddish brown, while the complex salt, $\left(^{RN}_{RN}>Cu<^{NR}_{NR}\right)Me_2$, is violet. Hence, it may be assumed that the change of light absorption which occurs when a simple salt (ion) is converted into a complex salt (complex ion) is connected with the increase of volume. The red violet-coloration which cyanuric acid gives in alkaline solution with cupric salts, which resembles the typical biuret reaction, is also dependent upon the formation of a complex copper alkali cyanurate, which has a constitution similar to that of the copper acid imide complex.

MISCELLANEOUS.

"Allen's Commercial Organic Analysis."—The Third Edition of Vol. II., Part 3, of this work is just ready for publication. The subjects dealt with are:—Acid Derivatives of Phenols, Aromatic Acids, Resins and Essential Oils. Much of the work of revision has been done by Mr. A. R. Tankard, F.C.S., Deputy Agricultural Analyst for Monmouthshire and the County Borough of Newport. With its issue the complete work in eight volumes may now be procured. The publishers are Messrs. J. and A. Churchill.

The Chemical Laboratory at Wiesbaden.—During the Winter Term, 1906-7, the Chemical Laboratory Fresenius was attended by 40 students. Of these, 27 were from Germany, 5 from England, 2 from Holland, 1 from France, 1 from Norway, 1 from Spain, 1 from the United States of America, 1 from Brazil, and 1 from East India, There were three assistants in the Instruction Laboratory, and twenty-three in the Versuchsstationen (private laboratories). To the certified staff of teachers belong the Directors, Geh. Regierungsrat, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Prof. Dr. med. G. Frank, Dr. L. Grünhut, Dr. R. Fresenius, and J. Huber (Architect). The next Summer Term begins on April 24th. During the Winter Term, 1906-7, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen) on behalf of trade, manufacture, mining, agriculture, hygiene, justice, and government.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Non-inflammable Alcohol.—Can any reader inform me if alcohol cao be made non-inflammable? The liquid so treated is not inteoded for humao consumption.—ALCOHOL.

MEETINGS FOR THE WEEK.

MONDAY, 15th.—Society of Arts, 8. (Cantor Lectures). "Detergents aod Bleaching Agents used in Laundry Work," by Prof. Herbert Jackson, F.I.C., &c.

TUESDAY, 16th.—Royal Institution, 3. "Wings aod Aeroplanes," by Prof. G. H. Bryan, F.R.S., &c.

——— Society of Arts, 8. "Joinery and Furniture Making," by A. Romney Green.

WEDNESDAY, 17th.—Society of Arts, 8. "Aërial Navigatioo," by Major B. F. S. Baden-Powell.

——— Microscopical, 8. "The Podura Scale," by E. M. Nelson. Exhibition of Slides of Foraminifera, by A. Earland.

THURSDAY, 18th.—Royal Institution, 3. "The Birth and Affinities of Crystals," by Prof. H. A. Miers, F.R.S., &c.

FRIDAY, 19th.—Royal Institution, 9. "Nerve as a Master of Muscle," by Prof. C. S. Sherrington, F.R.S.

SATURDAY, 20th.—Royal Institution, 3. (The Tyndall Lectures). "Studies in Magnetism," by Prof. Silvanus P. Thompson, F.R.S.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2473.

A NEW METHOD FOR THE SEPARATION OF THE YTTRIUM EARTHS.

By C. JAMES, A.I.C

In working up a specimen of gadolinite for the rare earths the remarkable fact was noted that the filtrate, after the beryllium separation by ammonium carbonate, contained a small quantity of rare earth oxalate, and that the nitrates obtained therefrom gave absorption bands which were very intense for erbium, while the holmium and dysprosium bands had grown very faint. The insoluble oxalates, which had been previously removed in the usual manner after conversion into the nitrates, presented the ordinary absorption spectrum of erbium, holmium, dysprosium, &c. It was at once apparent that either erbium oxalate was more soluble in beryllium oxalate, or else traces of the rare earth oxalates were thrown down by the ammonium hydroxide, re-dissolved in ammonium carbonate, and fractionated by means of heat. On boiling some of the oxalate material with a very concentrated solution of beryllium oxalate, it was found that the filtrate contained no erbium. The only alternative was that the fractionation was due to the ammonium carbonate.

Method of Separation.

Having determined by further experiment that the yttrium group oxalates were very soluble in ammonium carbonate, a careful search for the conditions bearing upon the separation was made, and the following method of procedure was found to give the best results:—

The oxalates freed from those earths giving insoluble double sodium sulphates are treated with a solution of ammonium carbonate made by saturating dilute (1 to 5) ammonium hydroxide with the solid salt. The whole is then well stirred, and the beaker placed in a water-bath; on warming, the whole enters into solution, forming a reddish yellow liquid. The temperature of the bath is then raised to boiling, when a precipitate soon appears. This is filtered off, and the filtrate re-treated in the same manner, and some five fractions thus obtained of approximately equal size.

Usually after the first two fractions have been taken the liquid rapidly loses carbon dioxide; although sometimes the ammonium carbonate begins to decompose even before the first precipitate forms.

The oxalate should be fresh and moist so as to easily mix up, and not contain more than traces of the cerium metals, for otherwise complete solution will not be obtained. After a little practice one is able to add just about the right amount of ammonium carbonate to dissolve the mixed oxalates, and thus avoid waste of this rather expensive reagent.

While the precipitates are forming the liquid should be well stirred so that the temperature is even throughout the mass; this applies specially to Fractions I. and II.

Results of Fractionation.

Fraction I. soon formed, and consisted of a crystalline powder with a faint pink tinge. One portion on igniting gave a yellowish oxide, and another on treatment with hydrochloric acid dissolved entirely with strong effervescence. The solution gave faint traces of the bands of didymium, the holmium and dysprosium bands were stronger than the erbium, but all the bands were weaker, showing a great increase in the percentage of yttrium. This first fraction consisted simply of carbonates.

Fraction II. appeared to be similar to Fraction I., except that it possessed more of a pink colour. The oxide was yellow, and original precipitate was again entirely soluble in hydrochloric acid. The solution gave no didymium absorption bands, while those of holmium, dysprosium, and erbium were stronger, and when compared with a solution of the gadolinite oxides it was seen that holmium and dysprosium had increased and erbium decreased.

Fraction III. took longer to form, and was heavier, of a rose colour, and was not entirely soluble in hydrochloric acid; so at this stage oxalates were being precipitated also. On ignition it gave a yellowish oxide, and the absorption bands of the solution were very much the same as the original material.

Fraction IV. required a considerable time to deposit, and was of a salmon colour. On heating, it gave a light coloured oxide with a faint yellow tinge, which, on dissolving in nitric acid, gave a very intense erbium spectrum; that of holmium and dysprosium had become weak.

Fraction V. obtained by evaporation to dryness and calcining gave a very dense oxide of a pink colour. It was soluble in strong nitric acid after heating for some time on the water-bath, giving a fine rose-coloured solution presenting an intense erbium spectrum, holmium and dysprosium being very weak.

This last fraction, usually smaller than the others, was converted into the oxalate, and again submitted to fractionation.

Fraction *a*. Coloured rose.
„ *b*. Coloured salmon.
„ *c*. Coloured delicate salmon.

The resulting oxide had a rose colour, which on being treated with nitric acid gave a very concentrated solution with only faint bands of holmium and dysprosium.

Fraction *d*, evaporated to dryness and ignited, gave a white oxide with a pink tinge.

This fraction was practically free from holmium and dysprosium. It gave erbium bands and also a thulium band in the red, and contained a fair amount of ytterbium and some thorium.

It will be seen by the above that the earths separate in the following order:—

Cerium group—yttrium, terbium—dysprosium, holmium—erbium—thulium—ytterbium.

Yttrium oxide was separated from the first fractions by the method of Muthmann and Rolig (*Ber.*, xxxi., 1718) as follows:—

The precipitate consisting chiefly of carbonate of yttrium was ignited, dissolved in nitric acid, the concentrated solution boiled, and a thick cream of magnesium oxide added until the liquid no longer gave absorption bands.

This well known method gives good results, although Dennis and Dales (*Journ. Am. Chem. Soc.*, xxiv., 428) were not successful in getting good separations by its aid. Their trouble undoubtedly lay in the fact that they employed the chlorides instead of the nitrates as recommended by Muthmann and Rolig.

While this method separates erbium, holmium, and dysprosium from yttrium, terbium clings, and for the final purification the chromate method of Muthmann and Bohm (*Ber.*, xxxiii., 49; Chemical News, lxxxi., 169) was employed, and a pure white yttria was easily obtained. The material separated from the major portion of the yttria by the above methods was again converted into oxalates and fractionated from ammonium carbonate solution.

It is always advisable to treat the oxides from minerals very rich in yttria by the above methods in order to remove the great excess of this earth before proceeding with the fractionation.

It will be seen that the "oxalocarbonate" method gives excellent results, the separation especially of pure erbium from holmium, dysprosium, and terbium being accomplished in a much shorter time than by any other known

method. The fractionation of holmium, dysprosium, and terbium is much slower than that of erbium, thulium, and ytterbium, the two last being found in the most soluble fractions.

Another advantage of this procedure lies in the fact that the last fraction is evaporated to dryness, and so no soluble elements are washed away as is the case where dilute solutions are employed.

This method has also been applied to some monazite residues which were on hand, and which were rich in terbium, holmium, and dysprosium, and contained besides erbium, yttrium, traces of samarium, and gadolinium. As before, the oxalates were very soluble, and gave dense precipitates, but the separation was not so immediate and complete as in the case of the gadolinite oxalates.

The colour of the oxides varied from orange-brown to pale yellow, the latter coming from the most soluble portion. In all of these separations it is highly important that in comparing fractions by colour and by the absorption spectrum the same acid be used as solvent, for otherwise erroneous conclusions may be reached owing to the colour and spectra varying in different compounds.

Complexity of Erbium.

One of the interesting and important results of this method of separation is the fact that the material known as erbium is in all probability complex, as was found to be the case with didymium. Differences in the absorption spectra of erbium from different sources are noticeable, and while it is too early to give any detailed description of the changes observed, it does seem well to call the attention of chemists working on the rare earths to this peculiarity. A considerable amount of gadolinite and xenotime is now being worked up and separated for purposes of future research.

In conclusion, I wish to thank Professor Charles L. Parsons for advice and the interest he is taking in the work, and acknowledge my indebtedness to the Welsbach Light Company for raw material received, through the courtesy of Dr. H. S. Miner.

New Hampshire College, Durham, N.H.
January 10th, 1907.

NOTE.—At the present time the author is investigating the bromates of the rare earths, which vary greatly as regards their solubility in water. After a few series of crystallisations of the bromates of yttrium, terbium, holmium, dysprosium, and erbium the least soluble crystals become white and the most soluble rose, while the intermediate are yellow. This together with the absorption spectra show that yttrium is the least soluble, while holmium and dysprosium come next, and then erbium, &c.

A paper will be published shortly giving the solubilities and other properties of these compounds together with the results of the fractionation of a large amount of material.

THE FRUIT OF *SMILACINA RACEMOSA* AND *BIFOLIA*.

By C. G. ELDREDGE and L. M. LIDDLE.

THE fruit of the *Smilacina racemosa* was gathered at Sylvan Beach, New York, on the shores of Oneida Lake, August 6th to 20th, 1906. The soil is composed very largely of sand, upon which is found a second growth of forest trees and shrubs. The region is not adapted to purposes of agriculture on account of the sandy character of the soil. The whole territory, comprising several square miles, was formerly the lake bottom at the period when the water was discharged through the Mohawk and Hudson Rivers. An elevation of the land took place by which the lake was projected farther north, and the water has since been discharged through the Oneida and Oswego rivers into Lake Ontario.

The fruit consists of berries which are borne on a racemose panicle. Most of them were gathered on August 6th while still green, because it was noticed that as they ripened the birds and fowls ate them, and many fell upon the ground and were lost. When first gathered, they were spherical in shape, green in colour with reddish stripes, somewhat of a pearly lustre, and about as large as medium size peas. They were picked attached to the upper portion of the stalk, and allowed to ripen slowly in the house. When ripened in this way or allowed to mature naturally, they possess a bright red appearance, and resemble currants. If the berries are kept for two or three hours in the air-bath at 110—120°, they assume the red appearance, and resemble the fruit that has come to its natural maturity. Three months after gathering, the berries weighed one-fifteenth of a grm. each; while those that had been secured the year before, after fifteen months, weighed one-twentieth of a grm. Each berry contains a relatively large nutlet of oily or resinous appearance. While this species is in general widely distributed, at Sylvan Beach the plants are restricted to a narrow area.

The Pulp.—There were on hand for this investigation 372 grms. of the air-dried fruit. We crushed 186 grms. in an ordinary meat grinder, which cut the husks and fleshy part of the berries and broke only a few of the nutlets.

The ground berries were placed in a 500 cc. flask which was fitted with an inverted condenser, and treated for three or four days on a warm water-bath until all colour was removed. Eight or ten successive portions of alcohol were required. The red extract was transferred to a larger flask, and the alcohol removed by distillation. The last 400 cc. of the distillate had a fragrant nut odour similar to that of the syrupy mass left in the flask.

A second portion of the uncrushed fruit was subjected to the alcoholic treatment with equally satisfactory results. The husks and nutlets were separated by placing them in water after the alcoholic extraction, and rolling them between the hands. This separated the nutlet from the rest of the berry, and allowed the lighter portions to be washed away in a manner similar to that of "panning."

A portion of the berries was treated with water, but this failed to remove the colouring matter and sugar as satisfactorily as did the alcohol.

A portion of the syrup in alcoholic solution was treated with a relatively large amount of purified bone-black for twenty-four hours on the water-bath, when it lost nearly all of its colour. This solution was afterwards used in testing for acids, salts, and the character of the sugars.

By holding one of the berries on platinum-wire in the flame, the characteristic colour of potassium was plainly visible. The same reaction was obtained by subjecting some of the thick syrup to a similar test.

We placed 2·175 grms. of the berry husks in a small platinum evaporating dish. On gently igniting these, a decided odour of scorched squash or pumpkin was discernible, which increased with the rise in temperature. The ash from the amount used weighed 0·03 of a grm. When a few drops of dilute hydrochloric acid were added to the residue, there was a brisk effervescence, probably from an original oxalate. The insoluble portion was filtered off, and to the filtrate were added a little alcohol and a few drops of a 10 per cent solution of platinic chloride. A microscopical examination showed the crystals to be octahedral in form. There was also a small quantity of iron in the ash. The filtrate from the potassium platinic chloride, after removing the excess of platinic chloride and treating with ammonia and ammonium oxalate, gave a white precipitate of calcium oxalate. The presence of this precipitate was confirmed in the usual way. The clear filtrate from the bone-black was tested for tartaric and oxalic acids. Both were found, and their presence was confirmed by several tests. Malic and citric acids seemed to be absent. As the alcoholic extract showed a strong acid reaction, the oxalates and tartrates doubtless exist in the form of the acid potassium salts. A trace of tannic acid was found. Of the two bases, calcium and

potassium, that were shown to be present, potassium exists in relatively greater quantities.

Sugars.—A portion of the filtrate from the bone-black was evaporated to dryness on the water-bath with constant stirring. 0·2 grm. portions were weighed out, and treated according to Sherman and Williams (*Journ. Am. Chem. Soc.*, May, 1906, xxviii., 629). The time of the first three trials, one and a-half, one and a-half, and one and a-quarter minutes, corresponds to fructose. Portions of 0·1 grm., 0·05, 0·01, and 0·005 were similarly tested and likewise shown to be fructose. The osazone was filtered off and purified by repeated crystallisations from alcohol. It melted at 204—205°, which is the melting point of both dextrose and lævulose. A microscopical examination of the crystals showed their identity with the osazone of the sugar found in urine. The time of the osazone formation of a large number of samples of the sugar was noted, all of which showed it to be fructose, or at least chiefly lævulose. The sugar is deliquescent, returning to a thick syrup on exposure to the air for a short time. That which was extracted by the water had an odour and taste similar to New Orleans molasses. The taste became astringent and bitter after the sugar had remained in the mouth a short time.

The Nutlets.—After removing the husks and the fleshy portion as indicated in the foregoing, the nutlets were dried in the oven. 186 grms. of the berries gave 55 grms. of the dried nutlets. These were very hard and tough, and could not be ground in a coffee mill or meat grinder. A heavy iron mortar and pestle could make no impression upon them. Finally, recourse was had to a rock crusher. By passing them through this ten or twelve times, a moderately fine powder resulted.

The crushed nutlets were placed in a Soxhlet extractor, and treated with ether. The finer portions of the powder persistently stopped up the syphon of the apparatus, so the whole was finally transferred to a 250 cc. flask fitted with an inverted condenser. The treatment was continued for seventy-two hours. This gave a light yellow liquid, and on distilling off the ether there remained a substance which on standing separated into a liquid and solid oil; only about 10 cc. of both were obtained. On placing them in a freezing mixture, no change was observed. They were then saponified by an alcoholic solution of caustic potash. The resulting soap was dissolved in water and decomposed with dilute hydrochloric acid. After crystallising from alcohol, a microscopical examination showed the presence of palmitic acid imbedded in a matrix of unchanged oil. Crystallisation from ether was no more satisfactory than from alcohol. Judging from the physical characteristics, the oils seemed to be palmitin and olein.

The residue of the nutlets from the ether extraction was dried, and then treated as were previously the whole berries with alcohol. After the alcohol was distilled off, there remained another portion of sugar. This on stirring crystallised readily, and by subsequent tests proved to be fructose. This sugar in small quantities had a taste resembling horehound candy, becoming bitter and astringent after remaining a short time in the mouth. The melting-point of the pure sugar was found to be 95°, which indicated that it was fructose.

The Ripened Fruit.—In Eastern Iowa, near the highway between Mount Vernon and Marion, on September 25, 1906, some of the fully ripened fruit was found still on the stalks. It seemed an interesting experiment to compare the berries developed naturally to full maturity with those which were picked quite green and allowed to ripen slowly like bananas on the stems. There were found to be 200 grms. available for this part of the work. Their weight corresponded with those of the earlier picking; each one-fifteenth of a grm.

These were treated with the same solvents, the pulp with alcohol and the crushed nutlets with ether, as the other fruit, and they gave the same substances with one additional, tannic acid. The presence of this was distinctly shown in the pulp by a number of tests. It seems quite probable that the tannin exists in the green berries in the form of a glucoside, which changes into the acid as the fruit ripens under normal conditions.

Smilacina Bifolia.

These were gathered at Sylvan Beach from September 10 to 30, 1906. They are much more widely distributed in that region than the *racemosa*. 400 grms. of the air-dried fruit were at hand. The berries are much smaller than those of the other species, averaging one-twenty-eighth of a grm. in weight.

The nutlets were equal in hardness and toughness to the *racemosa*, and yielded only to the persistent use of the ore crusher. The same acids, bases, and oils were found in this as in the other species.

Substances Found.

Acid potassium tartrate, acid potassium oxalate, tannic acid in the ripened fruit of both species.

A small amount of calcium oxalate in the husks. Fructose with possibly a little glucose in the husks and the fleshy part of the berries. Pure fructose in the nutlets. Olein and palmitin.

A small amount of gum in both species.

The berries of both species seem to possess the same general properties.

We desire to express our thanks to Dr. N. Knight for advice and assistance in this work.

Chemical Laboratory, Cornell College,
March 27, 1907.

A STUDY OF THE METHODS FOR THE DETERMINATION OF ESTERS, ALDEHYDES, AND FURFURAL IN WHISKY.*

By L. M. TOLMAN and T. C. TRESCOT.

In the course of an examination of a large number of whiskies made in the U.S. Bureau of Chemistry under the direction of H. W. Wiley, the following work on the methods for the determination of the ethereal salts, aldehydes, and furfural was undertaken, as the methods adopted provisionally by the Association of Official Agricultural Chemists, as published in *Bulletin* 65 of the Bureau of Chemistry were found to be unsatisfactory.

Determination of Esters.

The provisional method as adopted by the Association of Official Agricultural Chemists in 1903 for the determination of esters is as follows:—

Neutralise the residue left after distillation in the fusel oil determination with N 10 sulphuric acid and add an excess of 10 cc. of the acid. Allow to stand five minutes and make up to 200 cc. Titrate two portions of 25 cc. each, using as indicators methyl-orange in the first and phenolphthalein in the second. The difference gives the amount of alkali necessary to neutralise the organic acids in 25 cc. of the sample. By subtracting from this figure the number of cubic centimetres of alkali required for the free acids and multiplying the result by 0·0088, the number of grms. of ethereal salts (calculated as ethyl acetate) in 25 cc. of the sample is determined.

The distillation of fusel oil is conducted as follows:—Add a small quantity of alkali to 200 cc. of the sample under examination, and distil slowly, till about 175 cc. have passed over; allow the distilling flask to cool, add 25 cc. of water, and distil again till the total distillate measures 200 cc. It was found, however, that it was exceedingly difficult to carry out this method satisfactorily, and, further, that it was very inaccurate, not in reality giving any true ester value.

* From the *Journal of the American Chemical Society*, xxviii. No. 11.

The first objection is that the method does not state that sufficient alkali must be added in the distillation to completely neutralise the acids and saponify the esters. If this is not done, there is a loss of unsaponified esters. Some of the whiskies required as much as 10 cc. of normal alkali to 200 cc. to accomplish this result.

The second objection is the difficulty experienced in the double titration with methyl-orange and phenolphthalein in the dark coloured whiskies, it being practically impossible to get two titrations agreeing within a reasonable limit of accuracy. It was also found that there is a considerable loss of volatile esters, which come over in the first part of the distillate before they are saponified, even though there be sufficient alkali present, and it was found necessary to boil with a reflux condenser before beginning the distillation. The chief source of error, however, is in the action of the alkali on the caramel and invert sugar present in the whisky.

How much this error may amount to is shown in Table I., where caramel prepared from pure cane-sugar was treated in the following manner :—A weighed amount of caramel is placed in an Erlenmeyer flask and dissolved in 50 cc. of alcohol (50 per cent by volume). This is exactly neutralised with N/10 alkali, using phenolphthalein as an indicator, and then 10 cc. of N/10 alkali are added, the flask connected with a reflux condenser, and boiled for one hour, then cooled, and the excess of alkali titrated.

Table I. shows that, with 0·500 grm. of caramel per 100 cc., which gives a colour about equal to a dark coloured whisky, we would have 7·6 cc. N/10 alkali used up by the caramel, which would be calculated as esters. This would be as much as the volatile esters in most whiskies. If, however, there was also invert sugar present, a still larger error would be introduced, as is shown in Table II.

Table II. shows that invert sugar uses up the alkali to a greater degree than caramel. If this reaction of alkali with caramel and invert sugar were quantitative, the figure might have some value, but it is not, so that such a determination can have no value in the presence of these substances.

An illustration of this fact is shown in the results on some brandies (Table III.).

Table III. shows that the fixed esters increase with the sugar, and are, in fact, dependent upon its presence. If it were not for this fact the determination of fixed esters might be of some value, as the accompanying table on pure whiskies indicates (Table IV.).

It was evident from this work that the provisional method is unsatisfactory, and does not give an ester number. It was therefore necessary to determine the esters in a distillate which was prepared in the following manner :—Add 25 cc. of water to 200 cc. of the whisky or spirit to be examined and distil off 200 cc. into a flask guarded with a mercury valve to prevent loss of alcohol. Measure 50 to 100 cc. of this distillate into a flask, add a few drops of phenolphthalein, and exactly neutralise the free acid with N/10 alkali : add 25 to 50 cc. of N/10 alkali, stopper the flask, and allow to stand at room temperature for eighteen to twenty hours, then connect with a single tube condenser and heat nearly to boiling for one-half hour, cool, and titrate the excess of alkali with N/10 acid.

The number of cubic centimetres of N/10 alkali used in the saponification multiplied by the factor 0·0088 gives the amount of esters present as ethyl acetate. There should be a considerable excess of alkali to ensure the saponification being complete.

The esters may also be determined by connecting the flask with a reflux condenser, instead of allowing them to stand over night, and boiling for one hour, and if only a few determinations are to be made this will be found to be the most satisfactory procedure, but where a large number of determinations are to be made the first scheme is very satisfactory. It was found by experiment that standing over night with the excess of alkali ensured complete saponification of the esters without any danger of loss of the volatile esters.

TABLE I.—*Effect of Alkali on Caramel.*

Caramel.	Amount of N/10 alkali used up.	Time of boiling.
Grm.	Cc.	Hours.
0·050	0·70	1
0·100	1·85	1
0·150	2·70	1
0·200	3·60	1
0·250	3·80	1
0·250	4·60	2

TABLE II.—*Effect of Invert Sugar on the Alkali.*

Invert sugar.	Amount of N/10 alkali neutralised.	Time of boiling
Grm.	Cc.	Hours.
0·059	1·2	1
0·050	1·5	2
0·100	2·9	1
0·150	3·6	1
0·250	5·85	1
0·250	6·95	3

TABLE III.—*Relation of the Solids and Invert Sugar to the Fixed Esters.*

Solids.	Invert sugar.	Amount of N/10 alkali used by 100 cc.	Amount of N/10 alkali used by volatile esters in 100 cc.	Amount of N/10 alkali used by fixed esters in 100 cc.
Per cent.	Per cent.	Cc.	Cc.	Cc.
1·2658	0·845	40·4	10·0	30·4
1·1348	0·820	47·6	8·8	38·8
1·0640	0·685	36·2	6·4	28·8
0·9726	0·596	32·2	7·2	25·0
0·7774	0·500	26·0	7·6	18·4
0·6840	0·392	26·6	4·8	20·9
0·6070	0·313	25·0	3·0	22·0
0·0306	—	18·8	12·4	6·4
0·0200	—	14·2	11·4	2·8
0·0054	Trace	9·6	9·6	0·0
0·0052	,,	16·4	15·4	1·0
0·0042	,,	10·0	7·4	2·6

TABLE IV.—*Determination of Fixed Esters in Pure Whiskies.*

Solids (per cent).	100 cc. of whisky.	Cc. N/10 alkali used by volatile esters in 100 cc.	Fixed esters in 100 cc.
0·3264	27·30	8·0	19·30
0·1976	21·20	9·50	11·70
0·1840	18·6	8·00	10·60
0·1690	15·8	5·2	10·60
0·1620	15·10	7·10	8·00
0·1592	13·4	5·8	7·60
0·1356	19·70	7·70	12·00
0·1164	7·70	2·00	5·70
0·0496	6·60	1·80	4·50

The question as to whether complete saponification could not be obtained in the cold by standing eighteen to twenty hours at room temperature with the excess of alkali was thoroughly tested in the following manner :—Duplicates were measured into flasks and the excess of alkali added, and stoppered, and allowed to stand over night. In the morning one was titrated and the other was heated for one hour with the tube condenser on the water-bath, cooled, and titrated. In thirty cases there was no difference between these titrations, and the average on 171 determinations was for the cold titrations 4·1 cc. N/10 alkali for 50 cc. of sample, and 4·2 cc. N/10 for 50 cc. of the sample that was heated, which indicates that practically complete saponification takes place at room temperature, and that the heating for one hour is not necessary, but in a few cases the titration of the cold saponified sample would be low, showing that complete saponification had not taken place. In our experience, therefore, it is safer

to complete the saponification by heating as directed in the method.

The samples that were heated on the water-bath always had a little more colour than the samples which were not heated, indicating a little more resinification of the aldehydes, which may account for the slightly higher results obtained by heating.

In order to check up the method of distillation the esters were determined in some artificial brandies before and after distillation. The results of four determinations on the original showed that 9 cc. of N/10 alkali were needed to saponify the esters in 100 cc., while, according to the average on twenty determinations on the distillate, 8·9 cc. were required for 100 cc., which shows that where the esters present are ethyl acetate, as they were in this sample, all are found in the distillate.

This experiment was repeated on five samples of new colourless whiskies with the same result, showing that the method of distillation is satisfactory, and that the esters are distilled over completely, although this does not prove that in the old aged whiskies there are not formed esters which are non-volatile, but it is impossible to distinguish them from colouring-matters and resinous materials which are affected by boiling with alkali, as has been shown.

(To be continued).

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 171).

Part II.—Analysis of the Silver, Copper, and Tin Groups.

General Discussion.

A survey of the main features of the method adopted for the analysis of the hydrochloric acid and hydrogen sulphide precipitates may be obtained by referring to the "Tabular Outline" accompanying this chapter. Here only the modifications introduced into the process ordinarily followed will be discussed.

In the precipitation and analysis of the silver group the usual process has been adhered to, the only addition being a provision for the detection of thallium, by removing the lead with sulphuric acid and then adding potassium iodide.

In the directions for the precipitation of the copper and tin groups by hydrogen sulphide, especial attention is given to securing the proper conditions as to acid concentration and temperature for a satisfactory separation of these elements from those of the iron group; for indefiniteness in this respect is one of the most common sources of difficulty to the inexperienced analyst. In our process, as will be seen by reference to P. 21, it is directly to precipitate first from a hot moderately acid solution. The fairly large acid concentration has the advantage of preventing the precipitation by hydrolysis of basic salts of titanium, bismuth, and antimonous antimony, and of hastening the precipitation of the arsenic. The high temperature promotes the precipitation of arsenic, molybdenum, and platinum, and causes all the sulphides to separate in a more readily filterable form. The solution is, however, finally diluted so as to contain 4 cc. of hydrochloric acid of specific gravity 1·12 in 100 cc., and is saturated with hydrogen sulphide in the cold; for only with an acid as dilute as this, and then in the cold, is it possible to precipitate as little as 1 or 2 mgrms. of cadmium or lead. Attention may be called to our experiments described in the chapter on "Confirmatory Experiments and References," which show that under these conditions the separation is a remarkably satisfactory one—at any rate from a qualitative analysis point of view, since not only is the precipitation of the copper and tin groups complete, but 1 mgrm. of zinc, iron, or nickel is found in the filtrate, even when 500 mgrms. of cadmium, copper, or tin are present.

In the case of substances originally dissolved without the use of nitric acid, which may therefore contain tin or antimony in the stannous or antimonous state, the hydrogen sulphide precipitate is, as usual, treated with ammonium polysulphide. The separation of certain elements by this reagent is, however, far from complete. Thus copper and mercury dissolve in not insignificant quantity in the polysulphide; and tin may remain entirely undissolved, even when several mgrms. are present, if cadmium, copper, or mercury is also present in large quantity; moreover, gold, platinum, and the elements allied to them divide themselves between the residue and solution to so large an extent and to so different an extent in different combinations, as to make this reagent entirely unsatisfactory for separating these elements; and with molybdenum the solution is seldom complete, though a large proportion of it always dissolves. New experiments confirmatory of these already known facts will be found described below in the chapter on "Confirmatory Experiments." Yet in a scheme devoted primarily to the common elements there seems to be no alternative process of separation which, on the whole, is nearly so satisfactory; especially since it is not difficult to separate tin from the elements of the copper group in the course of the analysis of the latter, and since enough copper and mercury always remain undissolved by the ammonium polysulphide to enable as little as 2 mgrms. to be detected.

In the case of substances not completely soluble in water, the treatment with nitric acid, recommended in Part I., converts tin and antimony into the higher state of oxidation; and this makes it practicable, as our experiments have shown, to substitute ammonium monosulphide for the polysulphide in the case of such substances, which constitute by far the larger proportion of those ordinarily submitted to analysis. This has the advantage of not dissolving cupric and mercuric sulphides appreciably, thereby not only making the tests for copper and mercury more delicate, but also making it possible to decide with certainty from the appearance of the precipitate produced by acid in the ammonium sulphide solution whether or not any element of the tin group is present. The monosulphide has, of course, the same defects as the polysulphide in not completely extracting tin and the rarer elements, but not in any more marked degree when these elements are in the higher state of oxidation. This will be evident by reference to the "Test Analyses of the Tin Group."

Tabular Outline.

Table IV.—*Analysis of the Silver Group.*

Precipitate.—AgCl, Hg_2Cl_2, $PbCl_2$, *TlCl. Treat with hot water (P. 12).

Solution.—$PbCl_2$, *TlCl. Add H_2SO_4 (P. 13).

Residue.—AgCl, Hg_2Cl_2. Pour NH_4OH through the filter (P. 15).

Filtrate.	*Precipitate.*	Black residue.	*Solution.*
*Tl_2SO_4. Add KI (*P. 13a).	$PbSO_4$. Dissolve in $NH_4C_2H_3O_2$, add K_2CrO_4 (P. 14).	$HgNH_2Cl$ + Hg.	$Ag(NH_3)_2Cl$. Add HNO_3 (P. 15).
Yellow precipitate, *TlI.	Yellow precipitate, $PbCrO_4$.		White precipitate, AgCl.

* From the *Technology Quarterly*, xix., No. 3 September, 1906.

Tabular Outline (continued).

TABLE V.—*Analysis of the Copper Group.*

H_2S *Precipitate.*—HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, As_2S_5 (with As_2S_3 and S_2), Sb_2S_3, Sb_2S_5, SnS, SnS_2, *PtS_2, *Au and *Au_2S_{1-3}, *Se, *Te (and TeS_2 ?), *MoS_{2-3}. Digest with ammonium sulphide (P. 22).

Residue.—HgS, PbS, Bi_2S_3, CuS, CdS, [*PtS_2], [*Au and Au_2S_{1-3}], [*MoS_{2-3}]. Boil with HNO_3 (P. 23).

Residue.—HgS, SnO_2, *Au and *Au_2S_{1-3}, *PtS_2. Add Br_2 solution (P. 24).

Residue.—SnO_2. Dissolve in $(NH_4)_2S$ (P. 25). Unite with tin group (P. 41).

Solution.—Add KCl, evaporate to a small volume (*P. 24*a*).

Yellow precipitate, *K_2PtCl_6.

Filtrate.—Add NaOH and $H_2C_2O_4$, and heat (*P. 24*a*).

Purple precipitate, *Au.

Solution.—Add $SnCl_2$ (P. 24).

White or grey precipitate, Hg_2Cl_2 or Hg.

Solution.—Pb, Bi, Cu, Cd, as nitrates. Add H_2SO_4, evaporate, add water (P. 26).

White precipitate, $PbSO_4$. Dissolve in ammonium acetate, add K_2CrO_4 (P. 14).

Yellow precipitate, $PbCrO_4$.

Filtrate.—Add NH_4OH (P. 27).

Precipitate. $Bi(OH)_3$. Dissolve in HCl, evaporate, add to water (P. 28).

White precipitate, BiOCl. Add Na_2SnO_2.

Black residue, Bi.

Filtrate.—$Cu(NH_3)_4SO_4$ (blue), $Cd(NH_3)_4SO_4$.

To a small part add CH_3COOH and $K_4Fe(CN)_6$ (P. 29).

Red precipitate, $Cu_2Fe(CN)_6$.

White precipitate, $Cd_2Fe(CN)_6$.

To the remainder add KCN and H_2S (P. 30).

Yellow precipitate, CdS.

Solution.—$(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2SnS_3$, *$(NH_4)_2PtS_3$ (?), *$(NH_4)_3AuS_3$ (?), *$(NH_4)_2SeS_3$ (?), *$(NH_4)_2TeS_3$ (?) *$(NH_4)_2MoS_4$. Add HCl (P. 41).

Precipitate.—See Table VI.

TABLE VI.—*Analysis of the Tin Group.*

Precipitate from Ammonium Sulphide Solution.—As_2S_5, Sb_2S_5, SnS_2, *PtS_2, *Au_2S_{3-6}, *SeS_2 (?), *TeS_2 (?), *MoS_3. Heat with 10 cc. HCl, 1·20 (P. 42).

Solution.—$SbCl_3$, $SnCl_4$. Dilute to 50 cc., heat, and pass in H_2S (P. 45).

Orange precipitate, Sb_2S_3. Dissolve in HCl, add Zn and Pt (P. 46).

Black deposit, Sb. Treat with NaOCl.

Black deposit, Sb.

Solution.—$SnCl_4$. Cool, dilute, pass in H_2S (P. 47).

Yellow precipitate, SnS_2. Dissolve in HCl, add Zn (P. 47).

Grey deposit, Sn. Dissolve in HCl, add $HgCl_2$ (P. 47).

White precipitate, Hg_2Cl_2.

Residue.—As_2S_5, *PtS_2, *Au, *Se, *Te, *MoS_3. Dissolve in HCl and $KClO_3$, evaporate to a small volume (P. 43).

Yellow precipitate, *K_2PtCl_6. Dissolve in hot water, add KI (*P. 43*a*).

Dark red colour, *K_2PtI_6.

Filtrate.—H_3AsO_4, *$AuCl_3$, *H_2SeO_3, *H_2TeO_3, *H_2MoO_4. Add NH_4OH, NH_4Cl, and $MgCl_2$ (P. 44).

White precipitate, $MgNH_4AsO_4$. Dissolve in HCl, add H_2S (P. 44).

Yellow precipitate, As_2S_5, As_2S_3, and S.

Filtrate.—Heat with $H_2C_2O_4$, filter (*P. 43*b*).

Purple or dark yellow precipitate, *Au.

Filtrate.—Evaporate, add strong HCl and Na_2SO_3 (*P. 43*c*).

Red precipitate, *Se.

Filtrate.—Add water and KI (*P. 43*d*).

Black precipitate, *Te.

Filtrate.—Boil off SO_2, add KCNS and Zn (*P. 43*e*).

Deep red colour, *$Mo(CNS)_4$.

In the process of analysis of the copper group (see Table V.) the only important modification introduced has reference to the extraction of the tin, which may, as just stated, remain wholly in the residue undissolved by ammonium sulphide. The residue undissolved by nitric acid, which may consist of mercuric sulphide and metastannic acid, is treated with bromine water instead of with an acid oxidising mixture, in order to dissolve out the mercury and leave behind the tin, which can then be dissolved in ammonium sulphide and united with the main solution of the tin group.

For the analysis of the tin group various processes have been proposed, and are in general use. As will be seen from Table VI., the method of separation here adopted is based entirely on the different solubilities of the three sulphides of arsenic, antimony, and tin in hydrochloric acid of varying concentration. This process, which seems to have been first suggested for the separation of antimony and tin by Loviton (*Journ. Chem. Soc.*, 1888, liv., 992), and which has been utilised in part by Bailey and Cady in their text-book on qualitative analysis, we have somewhat developed by a detailed study of the best conditions for making it a good qualitative method. We believe this method is the one best adapted to the purposes of ordinary qualitative analysis, because of its great simplicity, and because of the fact that the tests, while being of sufficient delicacy to detect 1 mgrm. of any of these elements, do not have in the case of arsenic and antimony the extreme sensitiveness of the reduction tests based on the decomposition by heat of hydrogen arsenide and antimonide.

Of the rarer elements precipitable by hydrogen sulphide, provision has been incidentally made for the detection of all the more important ones, namely, for that of molybdenum, selenium, tellurium, gold, and platinum. The treatment with hot concentrated hydrochloric acid employed for separating the sulphides of antimony and tin from that of arsenic makes such provision comparatively simple; for the sulphides of all these rarer elements are left, with that of arsenic, together at one place in the scheme (except that gold and platinum may also remain in the copper group residue, and have to be tested for also in the analysis of that group). No attempt has been made to include the other so-called platinum elements, since the reliable detection of these can be effected only by a special and complicated process. These elements will be treated in the "System of Analysis including nearly all the Metallic Elements," which is being published in the *Technology Quarterly*.

(To be continued).

SEPARATION AND ESTIMATION OF BERYLLIUM.

By CHARLES L. PARSONS and S. K. BARNES.

The separation of beryllium from other elements presents little difficulty except in the case of aluminium and iron. It will invariably be found with aluminium in the last instance, and the problem therefore becomes the determination of beryllium in such a mixture.

Many methods for the separation of beryllium from iron and aluminium have been proposed, but the one most often used has been founded upon the solubility of its hydroxide in ammonium carbonate, which unfortunately dissolves also some of the hydroxides of aluminium and iron. Vauquelin (*a*) in 1798 first used ammonium carbonate, but his first separation depended upon the solubility of beryllium hydroxide in potassium hydroxide and its precipitation on boiling. Gmelin (*b*) and Schaffgotsch (*c*) both used this same method, but it is very far from being accurate. Sheerer (*d*) first proposed the separation of the last traces of iron from the ammonium carbonate solution by means of ammonium sulphide. Berthier (*e*) suggested the use of ammonium sulphite as a reagent, but the method was shown to be valueless by Böttinger (*f*). In 1850 Rivot (*g*) proposed the ignition of the oxides in a current of hydrogen whereby the iron was reduced to metal and could be dissolved out with dilute nitric acid or its mass determined by the loss of weight. Debray (*h*) developed a separation dependent upon the action of zinc on the mixed sulphates precipitating the aluminium as a basic sulphate, but the method was never made quantitative. Joy (*i*) made a comparative study of all methods proposed to his time. Gibbs (*k*), in 1864 for the first time, suggests the use of sodium fluoride to quantitatively separate aluminium from beryllium, and Pollok (*l*) shows that the fluoride separation is exceedingly sharp. Cooke (*m*), after reducing the iron in hydrogen, volatilises it in a current of hydrochloric acid. Havens and Way (*n*) accomplish the same result without previous reduction of the oxide. Rössler (*o*) succeeded in separating beryllium from small amounts of aluminium by precipitating with ammonium phosphate in the presence of citric acid. Vincent (*p*) uses dimethylamine to precipitate beryllium salts, and finds that the aluminium compound is soluble in excess of the reagent. Iron acts like beryllium. Renz (*q*) confirms this, states the same to be true of methyl-, ethyl-, and diethylamine, and claims the results to be quantitatively accurate. Zimmermann (*r*) in 1887 returns to the old potassium hydroxide and sulphite or thiosulphate method without any special addition. Scheier (*s*) in 1892, Atkinson and Smith (*t*) in 1895, and Burgass (*u*) in 1896 separated iron quantitatively from beryllium by means of nitroso-β-naphthol. Lebeau (*x*) precipitates the iron in nitric acid solution by ferrocyanide, removes the ferrocyanide by copper nitrate, and the excess of copper by hydrogen sulphide. Hart (*y*) removes the major part of both iron and aluminium by careful precipitation of the sulphates with sodium carbonate, the beryllium being the last to precipitate, owing to the great solubility of its own hydroxide in its own sulphate. Havens (*z*) separates beryllium from aluminium quantitatively by the insolubility of hydrous aluminium chloride in a mixture of hydrochloric acid and ether which has been saturated with hydrochloric acid gas. Haber and Van Oordt (*aa*) dissolve basic beryllium acetate in chloroform, leaving aluminium and iron acetates behind. Myers (*bb*) removes iron electrolytically from a slightly acid solution of the sulphates, using a mercury cathode. Parsons and Robinson (*cc*) separate beryllium basic acetate in a pure state from other acetates by means of its ready solubility in hot glacial acetic acid and comparative insolubility in the same reagent when cold.

Preliminary Investigations.

Some qualitative work done by one of us some months ago had developed the fact that beryllium hydroxide was readily, immediately, and apparently completely separated from aluminium and ferric hydroxides by boiling momentarily in a saturated solution of acid sodium carbonate. No trace of aluminium could be found in the separated beryllium compound by Havens's method (*dd*), and the white hydroxide of beryllium or its hydrochloric acid solution showed scarcely a trace of colour. The object of this investigation was to determine whether or not this reaction could be made strictly quantitative.

Solutions of pure aluminium chloride and pure beryllium chloride were made and analysed, and it was early apparent on attempting to get closely agreeing results by precipitating the beryllium as hydroxide with ammonia that some source of error existed. After some experimenting it was found that the beryllium hydroxide, when freed of the ammonium chloride present, passed into the colloidal condition on washing with pure water, and, indeed, much more rapidly than is known to be the case with aluminium. On adding a small amount of ammonium acetate to the wash-water the difficulty immediately disappeared, and no trouble was experienced in obtaining well-agreeing results even in fairly strongly ammoniacal solution. Small amounts of beryllium hydroxide also adhere tenaciously to the glass of the precipitating beaker,

and after as perfect mechanical removal as possible the beaker should be treated with a little dilute nitric acid, and the contained beryllium re-precipitated. Beryllium oxide obtained by blasting the hydroxide is somewhat hygroscopic, and should be weighed with due precautions.

References.

(*a*) Vauquelin, *Ann Chim. Phys.*, xxvi., 155.
(*b*) Gmelin, *Ann. Physik.*, l., 175.
(*c*) Schaffgotsch, *Ibid.*, l., 183.
(*d*) Scheerer, *Ibid.*, lvi., 479.
(*e*) Berthier, *Ann. Chim. Phys.*, [3], vii., 74.
(*f*) Bottinger, *Ann.*, li., 397.
(*g*) Rivot, *Ann. Chim. Phys.*, [3], xxx., 188.
(*h*) Debray, *Ibid.*, [3], xliv., 1.
(*i*) Joy, *Am. Journ. Sci.*, [2], xxxvi., 83.
(*k*) Gibbs, *Ibid.*, [2], xxxvii., 346.
(*l*) Pollok, *Trans. Roy. Dublin Soc.*, 1904, [2], 139..
(*m*) Cooke, *Am. Journ. Sci.*, [2], xlii., 78.
(*n*) Havens and Way, *Ibid.*, [4], viii., 217.
(*o*) Rössler, *Zeit. Anal. Chem.*, xvii., 148.
(*p*) Vincent, *Bull. Soc. Chim.*, xxxiii., 157.
(*q*) Renz, *Ber.*, xxxvi., 2751.
(*r*) Zimmermann, *Zeit. Anorg. Chem.*, xv., 285.
(*s*) Scheier, *Chem. Zeitung*, xvi., 420.
(*t*) Atkinson and Smith, *Journ. Am. Chem Soc.*, xvii., 688.
(*u*) Burgass, *Zeit. Angew. Chem.*, 1896, 596.
(*v*) Lebeau, *Comptes Rendus*, cxxi., 641.
(*y*) Hart, *Journ. Am. Chem. Soc.*, xvii., 604.
(*z*) Havens, *Am. Journ. Sci.*, [4], iv., 111.
(*aa*) Haber and Van Oordt, *Zeit. Anorg. Chem.*, xl., 465.
(*bb*) Myers, *Journ. Am. Chem. Soc.*, xxvi., 1124.
(*cc*) Parsons and Robinson, *Ibid.*, xxviii., 555.
(*dd*) Havens, *loc. cit.*

Separation and Determination.

The method is based on the total insolubility of aluminium and ferric hydroxide in a 10 per cent boiling acid sodium carbonate solution, and on the total solubility of beryllium hydroxide in the same. From the aluminium solution used the aluminium hydroxide was totally precipitated by the boiling hot saturated solution of acid sodium carbonate and the beryllium solution gave a perfectly clear solution with the same. The acid sodium carbonate employed was in the form of small crystals, and contained but a trace of the normal carbonate as indicated by phenolphthalein.

Portions of the solutions of beryllium and aluminium chlorides were weighed out containing amounts convenient to work with, and washed from the weighing-bottle into clean Jena beakers of 250 cc. capacity in which the separation was made.

The solution was made up to about 100 cc., neutralised as nearly as possible with ammonia, and 10 grms. of solid acid sodium carbonate added. If the solid carbonate is added to any but a cold solution spattering will take place.

The beakers were kept covered with watch-glasses to prevent loss of material by any escaping gas during the heating, and the solution was brought to a boil as quickly as possible, and allowed to boil not to exceed one minute. Carbon dioxide is not evolved very rapidly till the boiling temperature is nearly reached if the solutions are neutral, but evolution of gas must not be mistaken for boiling.

The solution was now set in cold water, and cooled, filtered, and washed two or three times with hot water. The precipitate was dissolved on the filter with as little as possible (1 : 1) hydrochloric acid, and run back into the same beaker in which the precipitation was first made, the solution made up to 100 cc., made neutral with ammonia, precipitated again with acid sodium carbonate as before, cooled, filtered, and washed with hot water, running both filtrates together. A cloudiness will be noticed in the combined filtrates after washing, which looks as if aluminium hydroxide were coming through, but this is not the case, the cloudiness being due to the dilution of the strong acid sodium carbonate solution with water. The aluminium hydroxide was again dissolved in (1 : 1) hydrochloric acid, precipitated with ammonia and determined in the ordinary way, as it was found that it was next to impossible to wash out all the acid sodium carbonate from the gelatinous precipitate.

The filtrate from the double precipitation, containing the beryllium in solution, was carefully acidified with strong hydrochloric acid in a covered beaker, as special care was required that the escaping gas should not cause mechanical loss. Just before neutralisation a portion of the beryllium was thrown down as hydroxide, but this immediately dissolved on addition of more acid. The solution was then boiled to remove carbon dioxide so that no ammonium carbonate should be formed, precipitated with ammonia, boiled, allowed to settle, and filtered, washing with ammonium acetate solution until free from chlorides. The beryllium hydroxide was ignited to constant weight, which is readily attained, and weighed.

Results follow :—

Al_2O_3 taken.	Al_2O_3 found.	BeO taken.	BeO found.	Total taken.	Total found.
0·1252	0·1266	0·0818	0·0810	0·2070	0·2076
0·1323	0·1336	0·0795	0·0781	0·2118	0·2117
0·0942	0·0957	0·0573	0·0563	0·1515	0·1520
0·0869	0·0881	0·0610	0·0588	0·1479	0·1469
0·0907	0·0945	0·0629	0·0594	0·1536	0·1539

The results are slightly too high in aluminium oxide and correspondingly low in beryllium oxide, although the totals found agree closely with the theoretical amounts. The aluminium hydroxide showed therefore, as was to be expected, a tendency to occlude some beryllium hydroxide. Washing the first and second precipitation with hot acid sodium carbonate solution was next tried, and this seemed to assist in removing the beryllium, although small amounts were still left behind in the aluminium hydroxide, as the following results will show :—

Al_2O_3 taken.	Al_2O_3 found.	BeO taken.	BeO found.	Total taken.	Total found.
0·0840	0·0849	0·0646	0·0642	0·1486	0·1491
0·0740	0·0749	0·0680	0·0676	0·1420	0·1425
0·2059	0·2055	0·0972	0·0977	0·3031	0·3032
0·6152	0·6167	0·0372	0·0348	0·6524	0·6515
0·1327	0·1346	0·3125	0·3107	0·4452	0·4453
0·1368	0·1386	0·3050	0·3031	0·4418	0·4417
0·6233	0·6250	0·0730	0·0714	0·6963	0·6964

Trials were made of heating the acid sodium carbonate solution in pressure flasks so that no carbon dioxide might escape, but the results were not satisfactory.

By the procedure so far followed the mixed hydroxides were first precipitated together in the cold, and the beryllium hydroxide dissolved in the boiling reagent. This would seemingly tend to allow the aluminium hydroxide to so enclose some of the solid beryllium hydroxide that the reagent could not act upon it. This was particularly the case when relatively large amounts of aluminium were present. To overcome this difficulty as much as possible, separations were tried by adding the boiling hot mixture of the chlorides to a nearly boiling solution of acid sodium carbonate containing enough of the reagent to make the mixed liquid an approximately 10 per cent solution. The whole was then brought to a boil, held there for half a minute, cooled, and treated as before. By this procedure only the aluminium was precipitated as hydroxide, and less beryllium was mechanically retained. Larger amounts of aluminium were used in this case than before, and as the results could be interpreted from the beryllium alone the aluminium was not weighed.

BeO taken.	BeO found.
0·1311	0·1307
0·1424	0·1415
0·2522	0·2515
0·0671	0·0664
0·0642	0·0631

To show the application of this same procedure in the presence of iron, ferric chloride was added in variable amounts, both large and small, to mixtures of aluminium and beryllium chlorides, boiled with a little nitric acid to ensure oxidation, and the whole treated as above. The combined hydroxides of iron and aluminium were several times the mass of the beryllium hydroxide, yet the separation was almost complete, and the resulting beryllium oxide was analytically pure.

BeO taken.	BeO found.
0·2152	0·2146
0·0911	0·0906
0·0825	0·0806
0·1020	0·0995

Considering the well known great tendency of gelatinous hydroxides like those of aluminium and iron to retain other substances which may be present, this separation of beryllium leaves little to be desired. Care must, of course, be exercised to bring the acid sodium carbonate quickly to a boil, and to boil for a moment only, for if too much carbon dioxide is lost the aluminium may partially pass into solution.

Conclusions.

Beryllium hydroxide must be washed with water containing an electrolyte to prevent the loss of colloidal hydrate through the filter.

Beryllium can be quantitatively separated from iron and aluminium by means of the solubility of its hydroxide in a boiling hot solution of acid sodium carbonate of approximately 10 per cent strength.—*Journal of the American Chemical Society*, xxviii., No. 11.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, April 8th, 1907.

Mr. R. J. Friswell in the Chair.

"*Observations on Cotton and Nitrated Cotton.*" By Henry de Mosenthal, F.I.C.

This paper is a continuation of one of the same title read on March 31st, 1904, before the London Section. It deals with the appearance of celluloses and nitro-celluloses in polarised light, their refractive indices and optical activity as well as densities. Fourteen samples of nitrated cottons of different degrees of nitration, different solubility and viscosity, three samples of nitrated wood cellulose, and two each of nitrated ramie and flax were examined. The appearance in polarised light was found to vary with the degree of magnification and the light used, fibres appearing differently when dry and when moistened. Various moistening liquids gave different results. The colours shown in polarised light under the same conditions seemed to be chiefly dependent on the material nitrated and the method of nitration. The densities of celluloses and of nitro-celluloses examined were found to be higher than those recorded in text-books. The densities of nitrated material in solution were also ascertained, and found to be higher than in the solid state. Observations of the refractive index of nitrated cotton in solution gave results which were not concordant, and therefore determinations were made on transparent films of nitrated cotton, ramie, and flax. The refractive index of cellulose was found by examining denitrated films, and then by placing fibres in a liquid of like refraction. Atomic refractions were applied to some of the proposed formulæ for cellulose, and showed that the cellulose molecule has no double bonds. Although for the present without stoichiometrical value, the dispersion was determined and the reciprocal of the relative dispersion calculated. The optical activity of various nitro-celluloses in solution was found to agree fairly well with the figures given by Vignon. The range of concentration within which clear solutions could be obtained made it impossible to establish constants. The paper concludes with a reference to work in progress with regard to the dialysis of nitro-cellulose and solution pressures generally.

NOTICES OF BOOKS.

Qualitative Analysis. By William Congle Morgan, Ph.D. (Yale). New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1906.

This book has the excellent object of imparting principles rather than facts to the student, and giving him a due idea of the relative importance of the facts he has assimilated in his elementary work, an idea which the majority of beginners lack to a very marked degree. The treatment is based upon the ionic theory of dissociation, and in the first or general part some fundamental principles are discussed, such as mass action, hydrolysis, oxidation, and reduction; some processes which are commonly employed in qualitative analysis are explained, and the theory of ionisation is gone into fairly fully. In the second part the classification of the elements according to the Periodic System is discussed, and the characteristic properties of the commoner members of the groups are described. In this part the knowledge the student will have acquired from his reading is worked in very well with his analytical work, which will thus be established upon a thoroughly sound basis. Systematic analysis is treated in the third part in a fairly advanced and very thorough manner, and the book will commend itself for those who want a work of reference perhaps more than a laboratory text-book, for which it is rather too discursive. However, the reason for every step taken is carefully explained, while excellent notes are given on the detection of interfering substances.

Handbook of Metallurgy. By Dr. Carl Schnabel. Translated by Henry Louis, M.A. Second Edition. Vol. II. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1907.

The second volume of the translation into English of Dr. Schnabel's valuable and comprehensive work on metallurgy deals with the metals zinc, cadmium, mercury, bismuth, tin, antimony, arsenic, nickel, cobalt, platinum, and aluminium, and describes fully the methods of extracting them from their ores, including those processes which are as yet of merely scientific interest as well as those practically employed. The physical and chemical properties of the metals are discussed, and also the composition of their alloys, and a short *résumé* is in each case given of the reactions of the metal and their most important compounds.

The Chemistry of Gas Manufacture. By W. J. Atkinson Butterfield, M.A., F.I.C. Fourth Edition. Volume I. London: Charles Griffin and Company, Ltd. 1907.

The revision of the second edition of this handbook entailed the addition of so much new matter that the author has thought it advisable to issue it in two volumes. The first of these deals with the materials and processes of gas manufacture, and already two editions of it have appeared, while Volume II. is to be published shortly. The first volume describes the properties and composition of peat, coal, oils, &c., while a short account is given of the analysis of coal. In this the author appears to have committed an error of judgment in assuming that the student would require no instruction in the method of carrying out combustions, which can hardly be regarded as very

elementary work, while on the other hand he takes the trouble to explain in detail the very simple process of finding the specific gravity of a solid, which the modern schoolboy surely has at his fingers' ends. The plant necessary for the manufacture of coal-gas is described with explanatory diagrams and illustrations, and methods of gas purification according to the scheme which is generally adopted in London is given full consideration. The manufacture of carburetted water-gas and oil-gas is discussed, and schemes for the enrichment of gas form the subject of the last chapter, which also goes shortly into questions connected with its storage and distribution, the author thinking it unnecessary to treat them in full, as properly speaking they belong to the province of the engineer.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 12, March 25, 1907.

This number contains no chemical matter.

No. 13, April 2, 1907.

Properties of a Body extracted from certain Alloys of Nickel and Tin.—Em. Vigouroux.—The alloys described in a previous article were submitted alternately to the action of hot nitric acid and fused caustic potash, with a final washing with dilute nitric acid. The compound NiSn (33·24 Ni, 66·76 Sn) was thus isolated. This body is generally obtained in the form of a silvery white crystalline powder, showing brilliant facets under the microscope. Its density (in melting ice) is about 8·44, the calculated number being 7·93; its formation is therefore accompanied by contraction. At red heat it is attacked by both chlorine and oxygen, to give chlorides and oxides of the two metals; the sulphides are also equally easily obtained. Hydrochloric acid, sulphuric acid, and aqua regia dissolve it completely. Nitric acid produces scarcely any effect, and the fused alkalis react very slowly. *Conclusions.*—1. Certain bronzes, with nickel substituted for copper, containing from 73·64 to 91·72 per cent tin, treated alternately with nitric acid and caustic potash, gradually lose in tin until a certain limit is reached, which is the same for all, of about 66·74 per cent, and corresponding to the formula NiSn. 2. This non-magnetic body, presenting the characteristics of a definite compound, is apparently the only substance which can be isolated from this class of alloys; in other words, the richest nickel-tin compounds would contain the metals combined in the proportions of 1 to 2.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 4, 1907.

Salts of Zirconium.—Arthur Rosenheim and Paul Frank.—The authors' earlier work has shown that, generally speaking, no compound of a tetravalent Zr····· ion can exist in aqueous solutions even if they are strongly acid, but usually only zirconyl salts of the divalent $ZrO^{\cdot\cdot}$-ion. Ruer has shown that zirconium sulphate, $Zr(SO_4)_2.4H_2O$, is not the normal sulphate of zirconium, but behaves like a complex zirconyl sulphuric acid, $ZrO(SO_4H)_2.3H_2O$. A normal nitrate, $Zr(NO_3)_4.5H_2O$, has been obtained by Paykull from solutions made strongly acid with nitric acid. The authors have continued these investigations with the following results:—The substances which separate from solutions containing large quantities of mineral acids were first studied, except the phosphates which form insoluble amorphous precipitates, and the above statements were confirmed. From solutions containing hydrobromic and hydrochloric acids the compounds $ZrOBr_2.8H_2O$ and $ZrOCl_2.8H_2O$ separate. From hot concentrated nitric acid solution the zirconyl salt, $ZrO(NO_3)_2.2H_2O$, crystallises, but if a solution of freshly precipitated zirconium hydroxide in nitric acid prepared at the ordinary temperature is evaporated at 15° *in vacuo* over phosphorus pentoxide and caustic soda large prisms appear. These are very hygroscopic, and give up nitric acid in dry air. They consist of Paykull's normal nitrate, $Zr(NO_3)_4.5H_2O$. Ruer's work with the sulphate was completely confirmed. Zirconyl salts in neutral aqueous solution are fairly rapidly hydrolysed, giving colloid zirconium hydroxide. Zirconyl nitrate when finely powdered dissolves after long boiling in absolute alcohol, and from this solution a white powder is precipitated by ether, $Zr_2O_3(NO_3)_2.5H_2O$. From aqueous solutions of the sulphate, by the addition of potassium rubidium or cæsium sulphate, crystalline precipitates of the composition $R_2Zr_2O_3(SO_4)_2$ can be obtained. These readily hydrolyse in pure water, and must therefore be re-crystallised from dilute alkali sulphate solution. No stable double salts can be prepared from zirconium nitrate. If oxalic acid is added to an aqueous solution of a zirconyl salt (chloride or nitrate) a gelatinous precipitate results soluble in excess of oxalic acid. If dilute sodium acetate solution is added the precipitate can be filtered, dried, and analysed. Its formula is $ZrO(C_2O_4).4H_2O$. When aqueous oxalic acid solution is added to zirconium hydroxide and boiled, an acid oxalate, $Zr(OH)(C_2O_4H)_3.7H_2O$, separates. The cautious addition of tartaric acid solution to a solution of zirconium oxychloride gives a precipitate of the composition shown by the formula $Zr_3(OH)_8(C_4H_2O_6).6H_2O$.

Zirconium Tetrachloride and Colloid Zirconium Hydroxide.—Arthur Rosenheim and Julian Hertzmann.—When an ethereal solution of benzoic acid ethyl ester is heated with zirconium tetrachloride, crystals having the formula $ZrCl_4(C_6H_5.CO_2C_2H_5)_2$ separate. Ketones and aldehydes also react with the tetrachloride, also salicylic acid and aldehyde, formic acid, acetic acid, &c. The compound with acetic acid consists of microscopic prisms easily soluble in water and alcohol, but insoluble in ether. It gives up acetic acid in the air, yielding zirconyl acetate, $ZrO(CH_3CO_2)_2$, which in moist air gives up more acetic acid, undergoing hydrolysis. Hydrolysis also occurs in aqueous solution, and colloid zirconium hydroxide is formed. After dialysing a 1½ per cent solution of zirconium acetate for about a week an absolutely clear solution is obtained; it coagulates on heating on a water-bath, and contains all its zirconium hydroxide in the colloid form; on addition of dilute potassium chloride solution and boiling, the zirconium chloride is precipitated quantitatively.

Reductions with Amorphous Phosphorus (II.).—Th. Weyl.—The action of amorphous phosphorus upon nitrobenzene in presence of alkali was investigated—(1) by means of experiments carried out at the ordinary pressure with a reflux condenser; (2) experiments at the ordinary pressure in which the reacting mixture was heated on an oil-bath with a reflux condenser; and (3) experiments in closed tubes at increased pressure. It was found that when nitrobenzene is allowed to drop into a boiling mixture of caustic soda, water, and red phosphorus, and the liquid is distilled in a current of steam, aniline and nitrobenzene are found in the distillate, and the nascent phosphine has undoubtedly acted as a reducing agent. If nitrobenzene is boiled for some time with the mixture generating phosphine—it is immaterial whether the pressure is raised or not—besides aniline the whole series of intermediate products between nitrobenzene and aniline is formed, viz., azoxybenzene, hydrazobenzene, and azobenzene. Large quantities of soluble substances, *e.g.*, phenols, are also formed. Thus the action of alkali and phosphorus upon nitrobenzene is essentially different from the action of water and phosphorus. The latter gives aniline, and under suitable conditions more than 80 per

cent of the theoretical yield; the former, on the other hand, acts as a feeble reducing agent, producing the intermediate products between nitrobenzene and aniline. The equations are :—

$$\text{I. } 2C_6H_5NO_2 + PH_3 = C_6H_5.N{<}\!\!\!

MEETINGS FOR THE WEEK

MONDAY, 22nd.—Society of Arts, 8. (Cantor Lectures). "Detergents and Bleaching Agents used in Laundry Work," by Prof. Herbert Jackson, F.I.C., &c.

TUESDAY, 23rd.—Royal Institution 3. "Stimulation, Luminous and Chemical," by Prof William Stirling, M.D., &c.

—— Society of Arts, 4.30. "Social and Economic Conditions in Australia," by the Hon. John Winthrop Hackett, LL.D.

WEDNESDAY, 24th.—Society of Arts, 8. "Rubber Cultivation in the British Empire," by Herbert Wright.

THURSDAY, 25th.—Royal Institution, 3. "Euripides and His Age," by A. W. Verrall, Litt.D.

FRIDAY, 26th.—Royal Institution, 9. "New Illuminants," by James Swinburne, F.R.S.

—— Physical, 5. "Electrical Conduction produced by Heating Salts," by A. E. Garrett. "Influence of Pressure upon Convection Currents, and a Criticism of J. Stark's Relation between Cathode Fall of Potential and Temperature," by W. S. Tucker. "Solenoids which are Turned by the Earth's Magnetic Field," by W. B. Croft. "Simple Apparatus for Mechanically Illustrating the Tangent and Sine Laws," by J. A. Tomkins.

SATURDAY, 27th.—Royal Institution, 3. (The Tyndall Lectures). "Studies in Magnetism," by Prof. Silvanus P. Thompson, F.R.S.

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Wanted, an ASSISTANT to the COUNTY ANALYST. Experience in analysis of Food and Drugs essential. Preference given to applicants possessing Institute of Chemistry qualification. Salary £120, increasing annually by £10 to maximum of £150. Forms of application, and particulars of duties and terms of engagement, may be obtained at my office, and will be forwarded on receipt of a stamped addressed foolscap envelope.

Applications (endorsed "Analytical") must be upon the form provided, and must reach me not later than 10 a.m. on TUESDAY, the 7th day of MAY next.

Canvassing in any form will be a disqualification

Dated this 17th day of April, 1907.

N. J. HUGHES-HALLETT,
Clerk of the Derbyshire County Council.

County Offices, Derby.

COUNTY OF LONDON.

The LONDON COUNTY COUNCIL invites Tenders for the Supply of 4200 Tons of PROTOSULPHATE of IRON (Commercial Green Vitriol) to the Barking and Crossness Main Drainage Outfall Works.

Tenders, which must be upon the printed forms to be obtained upon application to the Council's Chief Engineer, at the County Hall, London, S.W., must reach the Clerk of the Council not later than 10 a.m. on TUESDAY, APRIL 30th, 1907, and must be marked "Tender for Protosulphate of Iron." The Council does not bind itself to accept the lowest or any tender.

Full particulars, and also information as to the conditions to be observed by tenderers, will be given in the "London County Council Gazette" of April 15th, 1907. The Gazette, which is published weekly, contains particulars of all Tenders invited by the Council, and can be obtained from Messrs. KING & SON, 2 & 4, Great Smith Street, S.W., price 1d. (post free 1½d.) an issue, or for the whole year a prepaid subscription of 6s. 6d.

G. L. GOMME,
Clerk of the London County Council.

County Hall, Spring Gardens, S.W.,
April 11th, 1907.

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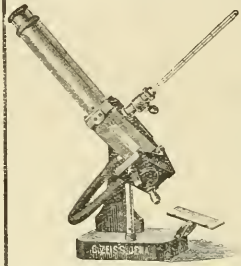

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THE WHEAT PROBLEM:

Based on Remarks made in the Presidential Address to the British Association at Bristol in 1898.

REVISED WITH AN ANSWER TO VARIOUS CRITICS

By SIR WILLIAM CROOKES, F.R.S.

With Two Chapters on the Future Wheat Supply of the United States, by MR. C. WOOD DAVIS, of Peotone, Kansas, and the HON. JOHN HYDE, Chief Statistician to the Department of Agriculture, Washington.

SECOND EDITION.

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CHEMICAL NEWS OFFICE.
16, NEWCASTLE ST., FARRINGDON ST., E.C.

THE CHEMICAL NEWS.

Vol. XCV., No. 2474.

ON THE CALCULATION OF PHYSICO-CHEMICAL CONSTANTS.

By H. STANLEY REDGROVE, F.C.S.

It has been found that the "ethylene" linkage exerts an influence on certain physico-chemical properties (*e.g.*, molecular refractivity, heat of combustion, &c.); it is therefore probable that the ordinary C.C link has also some influence; for example, the value of :C: in CH_4 is different from its value in C_2H_6; similarly the values of 6:C: in cyclo-C_6H_{12} and normal-C_6H_{14} are also different; at least the opposite may not be assumed. It is also most probable that the value of H. in H_2 is not the same as that of H. in an hydrocarbon.

This being so, the alleged atomic physico-chemical constants are incorrect, and, so far as our present knowledge goes, unobtainable.

The proof of this statement in the case of carbon and hydrogen follows. The hydrocarbons only have been considered, but the method may similarly be applied to other compounds.

Nevertheless, the examination of physico-chemical constants does show us the tenability of any particular formula for a body; the method of application is also outlined hereinafter.

Let H be the value of an H atom and the link joining it to C.

Let C be the value of a C atom, not including the value of its links.

Let L_1, L_2, and L_3 be the values of the C.C, C:C, and C:C links respectively.

If the constants for methane and three other hydrocarbons (one of each of the ethane, ethene, and ethine groups) are found experimentally, the value of the following may be calculated:—

$2H - L_1 = \beta$, $4H - L_2 = \gamma$, and $6H - L_3 = \delta$, and the value of $C + 4H = \alpha$ is known.

If a larger number of experimental results are found, a mean may be struck and greater accuracy obtained.

It is proposed to call the above the "fundamental constants" (for C and H).

We have here four equations involving five unknowns; these cannot be solved unless another equation not derivable therefrom can be obtained.

To see if this be possible it is necessary to develop a general expression for all hydrocarbons.

$nC + (2n+2)H + (n-1)L_1$ represents all open chain saturated hydrocarbons. The removal of 2H causes the replacement of a C.C link by a C:C link; thus, $a(2H + L_1)$ may be replaced by aL_2.

$nC + 2(n+1-a)H + (n-1-a)L_1 + aL_2$ represents therefore all open chain hydrocarbons not containing C:C links. These are obtained by replacing $b(4H + L_1)$ by bL_3.

$nC + 2(n+1-a-2b)H + (n-1-a-b)L_1 + aL_2 + bL_3$ represents therefore all open chain hydrocarbons.

Ring hydrocarbons can be obtained by the replacement of $2pH$ by pL_1.

$nC + 2(n+1-a-2b-p)H + (n+p-a-b-1)L_1 + aL_2 + bL_3$ is therefore a general expression for all hydrocarbons.

$$\begin{aligned} &nC + 2(n+1-a-2b-p)H + (n+p-a-b-1)L_1 + aL_2 + bL_3 \\ &= (nC + 4nH) + [(n+p-a-b-1)L_1 - 2(n+p-a-b-1)H] \\ &\quad + (aL_2 - 4aH) + (bL_3 - 6aH) \\ &= n\alpha - (n+p-a-b-1)\beta - a\gamma - b\delta. \end{aligned}$$

Therefore the expression for any hydrocarbon can be expressed in terms of the fundamental equations; consequently, no equation not derived therefrom can be obtained; therefore the equations are not capable of solution; that is to say, neither the atomic physico-chemical constants nor the value of the carbon linkages can be obtained.

The proof can be extended to other compounds.

The above identity enables us at once to write the formula of any hydrocarbon in terms of the known fundamental constants, and the theoretical value thus obtained can be compared with the value found experimentally.

As an example, the interpretation of the heat of combustion of benzene is appended, as this is a contested point. This method it will be noticed is vastly different from the forcing of a before-conceived result so often adopted.

From the heats of combustion of various hydrocarbons (Thomsen) the "fundamental constants" are found to be: $\alpha = 211{\cdot}9$ Cals., $\beta = 53{\cdot}5$ Cals., $\gamma = 90{\cdot}9$ Cals., $\delta = 114{\cdot}4$ Cals.

Kekulé's formula for benzene is represented by—

$$6C + 6H + 3L_1 + 3L_2 = 6\alpha - 3\beta - 3\gamma = 838{\cdot}2 \text{ Cals.}$$

Ladenburg's formula for benzene is represented by—

$$6C + 6H + 9L_1 = 6\alpha - 9\beta = 789{\cdot}9 \text{ Cals.}$$

Heat of combustion for benzene found by Thomsen is 788 Cals.

It must not be concluded that these facts are totally in favour of Ladenburg's formula, for the following reasons:

1. Owing to experimental difficulties we cannot place very great reliance on the experimental data.

2. Claus's old diagonal formula is also represented by $6C + 6H + 9L_1$.

3. It is not inconceivable that some other little known form of linkage (such as the central bonds) may not give an equally good theoretical value.

The Polytechnic, Regent Street, W.

AN INVESTIGATION TO DETERMINE THE PAPER-MAKING QUALITIES OF SHORT COTTON FIBRES.

By CLAYTON BEADLE and HENRY P. STEVENS.

The ultimate fibres of those materials used in the manufacture of the very best classes of papers, notably cotton, linen, hemp, ramie, manilla, &c., are under ordinary circumstances reduced in length in the process of manufacture, however carefully the material is manipulated with the object of preserving the length of the fibre. From a careful investigation of this subject, by taking measurements of the length of the fibres at different stages of the beating, as in the case of flax, hemp, cotton, and linen rags, the authors were led to conclude that it is impossible to preserve the ultimate length of the fibre; thus, in the case of flax fibre, for instance, as used in the manufacture of the strongest papers now produced, each ultimate fibre is reduced by being cut into at least four or five pieces before being reduced to the condition of pulp. This, moreover, is the prevailing opinion and experience of practical paper-makers, but it has hitherto lacked evidence in the shape of actual measurements under the microscope. The authors have, however, recently discovered that under certain conditions the cotton fibre can be reduced to pulp with little or no reduction in the initial length of the ultimate fibre.

For the purposes of this investigation a short-fibred cotton was selected, the cotton chosen being that which is partially removed by delinters from cotton-seed after the ginning operation. This fibre was boiled under pressure in a Jena beaker placed in a digester; the conditions of the boiling being varied to determine the most favourable conditions for the production of a product available for paper-making. The results of these digester trials are summarised in Table I. The time taken to reach the pressure mentioned on the table is about one hour. The time

TABLE I.—*Summary of Boiling Trials.*

No.	Date.	Amount taken, air dry.	Pressure.	Time.	NaOH on fibre.	NaOH on solution.	Bleach on fibre.	Yield of bleached half-stuff, air-dry.	Ether extract.	Alcoholic extract.	Total extract.	Ash.
		Grms.	Lbs.	Hours.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1.	5/12/06	100	15	4	8	1	2·5	—	0·17 (*a*)	0·53 (*b*)	0·7	0·5
2.	—	100	15	4	8	1	2·5	—	0·22 (*a*)	0·54 (*b*)	0·76	—
3.	—	195	15 to 56	1½ to 3	10	2	2·5	—	0·11 (*b*)	0·50 (*a*)	0·61	0·48
4.	12/2/07	300	15 to 56	1 to 3	10	2	2·5	67·0	0·116 (*a*)	0·41 (*b*)	0·526	0·24
5.	13/2/07	300	45	4	10	2	2·5	68·0	0·15 (*c*)	—	—	0·4
6.	14/2/07	300	45	4	10	2	2·5	70·0	0·126 (*d*)	—	—	0·4
7.	15/2/07	300	45	4	10	2	5·0	—				
8.	18/2/07	300	45	4	10	2	5·0	66·3				

(*a*) First extraction. (*b*) Second extraction. (*c*) Paper A. (*d*) Paper B.

TABLE II.—*Lengths of Fibres.*

Boiled and bleached cotton, before beating.			Paper A.			Paper B.		
Mm.	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
3·6	0·9	1·2	2·9	1·4	2·4	3·1	1·7	2·4
1·7	2·1	1·9	1·4	1·7	2·1	1·2	1·7	4·0
0·9	2·4	4·3	2·4	1·2	1·2	1·2	1·7	0·9
2·1	2·1	3·8	3·8	3·1	2·9	0·9	1·9	0·5
1·7	1·9	1·9	2·9	1·4	4·8	2·9	2·1	1·0
3·1	2·1	2·6	1·4	1·4	1·7	1·4	4·0	1·7
1·9	5·0	5·0	4·3	2·1	2·6	1·0	2·1	1·7
4·3	0·7	0·7	1·0	2·4	0·9	0·9	1·7	0·7
2·9	1·4	2·4	1·2	1·0	2·4	1·2	0·9	0 3
1·0	1·4	1·4	0·7	1·7	2·6	1·2	3·3	4 0
4·5	3·3	0·7	4·8	2·4	0·7	1·0	1·0	1·2
1·2	4·5	1·9	3·6	3·8	1·7	3·3	1·4	0·7
3·1	0·5	3·6	0·7	3·1	3·6	2·4	0·7	0·9
1·4	2·1	1·0	1·2	1·7	1·9	1·9	0·5	1·0
1·2	3·2	0·5	3·1	2·4	1·2	2·1	1·4	1·7
Mean .. .. .. 2·31	2·25	2·19	2·36	2·05	2·28	1·71	1·74	1·51
Mean of three columns =	2·25			2·20			1·65	

TABLE III.

	Mean lengths of fibre from 45 readings.	Reduction in length of fibre on beating.	Calculated number of fibres cut during beating.
		Per cent.	
Boiled and bleached cotton, before beating	2·25	—	—
Boiled and bleached cotton, when beaten for Paper A ..	2·20	2·2	1 in 23
Boiled and bleached cotton, when beaten for Paper B ..	1·65	26·6	1 in 3

TABLE IV.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
							Per cent.	Mm.	Lbs.	Lbs.	Lbs.	Lbs.
Sample A.	1.	1·05	3·17	2·12	0·106	1·156	9·2	0·096	15·92	16·58	9·11	0·99
,,	2.	1·07	3·05	1·98	0·099	1·169	8·5					
,,	3.	0·92	1·61	0·69	0·0345	0·9545	3·7	0·084	10·35	12·32	4·88	1·32
,,	4.	1·07	2·07	1·00	0·050	1·120	4·5					
,,	5.	1·06										
Sample B.	1.	1·00	1·69	0·69	0·0345	1·0345	3·3					
,,	2.	1·17										
,,	3.	1·20	2·23	1·03	0·0515	1·2515	4·1					
,,	4.	1·32	1·86	0·54	0·027	1·347	2·0					
,,	5.	1·26	2·10	0·84	0·042	1·302	6·4	0·084	15·30	18·59	6·59	1·03

Headings to Columns of Table IV.

1. Reference No. of sample, &c.
2. Air-dry weight of water-leaf.
3. Wet weight after dipping in 5 per cent gelatin solution.
4. Weight of 5 per cent gelatin solution taken up by water-leaf.
5. Air-dry weight of gelatin taken up by paper.
6. Air-dry weight of paper after sizing with gelatin.
7. Percentage of air-dry gelatin calculated on air-dry weight of sized paper.
8. Thickness (in mm.) of paper from average of five thicknesses, measured with fraction micrometer.
9. Mean strength of paper after sizing, being the result of two tests in each direction of the web.
10. Mean strength, corrected to 0·1 mm. thickness.
11. The additional strength due to sizing with gelatin (expressed on sheets 0·10 mm. thickness).
12. Increase in strength due to gelatin after deducting the strength due to water-leaf and reducing to strength per each 1 per cent gelatin on paper 0·10 mm. thickness.

of boiling is reckoned from the time the recorded pressure is reached. The percentage of soda on the weight of the fibre, as well as the strength of the soda solution, is stated on the table.

After blowing off and discharging from the boiler, the product was in each case thoroughly washed on a wire sieve and then mixed with a solution of bleach powder equal to twenty times the weight of the fibre and left until a good white colour was produced. The product was then thoroughly washed, carefully bone-dried, and, after sufficient exposure to the air, was weighed in its air-dry form, from which weight the percentage yield was calculated. The yield was found to vary between 80 and 66 per cent, according to the quality of the raw fibre, and the air-dry moisture of the bleached product to be about 7 per cent. The air-dry bleach fibre was extracted for four hours with ether in a Soxhlet and subsequently for four hours with alcohol, the results of which tests are recorded in Table I., together with the percentage of ash found in the bleach product.

The product from boilings 5, 6, and 7, after thorough mixing, was beaten in a small hollander of 200 grms. capacity and converted into paper. The first lot (A) was beaten with the object of conserving the length of the fibre as far as possible; the second lot (B) was beaten so as to somewhat reduce the length of the fibre.

The beating of A was started at 11 a.m. with the "roll" off the plate; the roll was lowered just to brush the fibres at 11.30 a.m.; at noon, when the noise of "brushing" had disappeared, the roll was further lowered so as to "brush" again, and left until (at 1 p.m.) fibres were completely separated. Total time in beater was two hours.

The beating of B was started at 2.10 p.m. with roll just brushing; the roll was further lowered (at 3.10 p.m.) so as to brush harder; at 3.30 p.m. the roll was further lowered, so as to just touch the plate and reduce length of fibres; and at 4 p.m. was further lowered, so as to beat harder, and so left until finished at 4.10 p.m. Total time in beater was two hours.

The beaten stuff A was run off on Marshall's miniature paper machine, which is a Fourdrinier paper machine complete in every detail. The behaviour of the stuff was very carefully watched. The stuff worked very "free" on the machine, *i.e.*, it parted very readily with its water, as a paper would do in the manufacture of blottings.

In the case of B, when run on the paper machine it was observed that the pulp worked sufficiently "wet" for all ordinary purposes of manufacture, and held the water up to the "dandy," so that the fibres could be well knitted together by the shake of the paper machine. Both papers looked well.

An average sample of the cotton fibre before beating was carefully secured from different parts of the bulk and intimately mixed. A number of fields were examined under the microscope, from which measurements of length were made, as shown in the first three columns of Table II.

Papers A and B were carefully reduced to the condition of pulp without reducing the length of fibre, and similarly mounted for measurement under the microscope, the results of which are also given on Table II.

Each set of measurements consists of three columns of fifteen measurements each. The average of each column differs only slightly. At the bottom of the table is given the figure for the forty-five readings recorded in each set.

Table III., which is prepared from above averages, shows that the reduction of length by beating in the case of A is practically nil, and in the case of B only about 27 per cent. From these figures it is evident that, in the case of paper A, only 1 fibre in 23 is cut by the beater knives; and, in the case of B, about 1 in each 3 fibres. Contrast this with the beating of ordinary cotton and linen rags for the production of "long stuff," where each fibre is cut on an average into five or ten pieces. These results prove to the authors' satisfaction that such short-fibred cotton can be reduced to the condition of pulp without reducing the length of the fibres; or, in other words, the ultimate fibres can be separated from one another and suspended in their watery medium for conversion into paper without being cut asunder. This, however, has never in the authors' judgment been done in conversion of long-fibred waste cotton into beaten stuff, nor is it possible to do so in the conversion of cotton rags into pulp, because, during the process of unravelling the latter or of undoing the work of the spinning and weaving operations to secure the suspension of the individual ultimate fibres in their watery medium, it is impossible to avoid the cutting asunder of the ultimate fibres into several individual pieces. It is noteworthy that, by careful brushing in the beater and by avoiding the beating operation proper and by using short fibred cotton in the manner above described, paper can be produced consisting of intact ultimate cotton fibres of such length that they are suited to the work of the papermaker. The authors regarded it of interest to examine such paper for physical qualities.

Accordingly, unsized paper from papers A and B were submitted to physical tests for strength, with the results as follow:—

Unsized paper A and B—

	A.	B.
Mean strength of machine direction (lbs.) ..	9·0	10·0
Mean strength of cross direction (lbs.) ..	3·5	6·25
Mean of both directions	6·25	8·12

Mean thickness of five sheets .. .. .. { A = 0·084 mm. B = 0·074 „

Mean strength of each paper corrected to 0·1 mm. thickness .. .. { $A = \frac{6·25 \times 0·100}{0·084} = 7·4$ lbs. $B = \frac{8·12 \times 0·100}{0·074} = 11·0$ „

Five sheets of A and B were impregnated with a 5 per cent solution of gelatin at 110° F., containing a small amount of alum, and passed between squeezing rollers to squeeze out the excess and hung up to air-dry, after the manner employed for tub sizing in the paper mill; the sheets were weighed immediately before and after sizing, from which the amount of gelatin, as retained by the air-dry paper, was calculated.

Certain of these sheets—A1, A3, and B5—were tested for strength, total stretch, and permanent stretch, with the results as follow:—

Sized paper (A1) tested for strength as follows—

Machine direction.	Lbs.	Cross direction.	Lbs.
1	19·6	3	12·0
2	19·5	4	12·6
Mean ..	19·55		12·3

Mean of the two directions .. .. .. = 15·92 lbs.
Average thickness of five sheets .. .. = 0·096 mm.
Mean strength per 0·10 mm. of thickness = 16·58 lbs.

Sized paper (A3) tested for strength, total stretch, and permanent stretch as follows:—

		Strength. Lbs.	Total stretch. Per cent.	Permanent stretch. Per cent.
Machine direction ..	1.	13·7	7·6	3·0
	2.	14·3	8·4	4·0
Mean		14·0	8·0	3·5
Cross direction	3.	6·3	7·2	3·8
	4.	7·1	9·4	5·0
Mean		6·7	8·3	4·4
Mean of both directions ..		10·35	8·15	3·95

Average thickness of five sheets .. .. .. 0·084 mm.
Average strength of both directions of sheet per 0·10 mm. thickness .. .. 12·32 lbs.

Sized paper (B5) tested as follows:—

		Strength. Lbs.	Total stretch. Per cent.	Permanent stretch. Per cent.
Machine direction ..	1.	18·2	8·0	4·2
	2.	16·7	9·4	4·6
Mean		17·45	8·7	4·4
Cross direction	3.	12·4	12·0	6·0
	4.	11·8	11·6	5·2
Mean		12·1	11·8	5·6
Mean of both directions ..		14·77	10·25	5·0

Average thickness of five sheets .. .. .. 0·084 mm.
Mean strength per 0·01 mm. thickness .. 17·59 lbs.

For purposes of comparison, the strength is finally expressed on paper of 0·1 mm. thickness and 25 mm. wide. Tests on the water-leaf papers show that paper with the short fibre has the greater factor of strength, due no doubt to the fact that the hydration of the fibre from the extra beating has increased its felting qualities. Here we have an exemplification of the apparent anomaly of increase in strength accompanying decrease in ultimate length of fibres. Column 10 gives some idea of the relative strengths of these papers, and goes to show that, in the case of B, although the ultimate fibre is reduced in length, yet it gives a greater breaking strain than unreduced fibre A3 for papers of the same thickness; and, furthermore, in the case of A1 and A3 (Columns 8 to 10), it appears that a paper of greater thickness gives a greater factor of strength.

This latter confirms the observations made by one of us as applied to papers consisting of pure linen, namely, that the greatest factor of strength is not obtained on the thinnest papers, but on fairly thick papers (Beadle, "The Fibrous Constituents of Paper," *Technics*, vol. ii., p. 254). Furthermore, it will be noticed (Column 12) that the influence of gelatin sizing is to increase the factor of strength per unit of added gelatin in an inverse ratio to the amount of gelatin. This confirms our previous observations that such is the case provided the amount of gelatin added is not too small (Beadle and Stevens, "The Influence of Sizing upon the Strength of Papers," *Journ. Soc. Chem. Industry*, vol. xxiv., p. 775).

The investigation is a somewhat difficult one, and requires further research on these points, but it goes to show without doubt that, with short-fibred virgin cotton, consisting largely of fibres without collapsed walls and twists and no central canal, excellent papers can be produced with little or no reduction in ultimate length of the fibres, and that such papers give a fair strength, equal at least to those from ordinary rags, and that the gaining in strength due to the sizing of gelatin is very marked. Furthermore, it shows that if such fibres are somewhat reduced in length by the beating, they behave on the Fourdrinier machine like those prepared from rags, and possess excellent felting qualities; in fact, the paper produced from such a material is, in the authors' opinion, as good in texture, appearance, and other qualities as that produced from cotton rags as used in the manufacture of high quality rag-papers.

The authors wish to express their indebtedness to Messrs. T. J. Marshall and Co., of Stoke Newington, for the use of their miniature beater and paper machine for the purpose of this investigation, and to their pupil, Mr. H. C. Potter, for his assistance in connection with the chemical tests and microscopical examinations.

Royal Institution.—On Saturday next, May 4th, at 3 o'clock, Professor W. C. McIntosh begins a course of two lectures on "Scientific Work in the Sea Fisheries." The Friday Evening Discourse on May 3rd will be delivered by Sir James Crichton-Browne on "Dexterity and the Bend Sinister," and on May 10th by Signor Comè Giacomo Boni on "Recent Excavations on the Forum Romanum and the Forum Ulpium." The Annual Meeting will be held on May 1st at 5 o'clock.

THE ELEMENTS OF THE YTTERBIUM GROUP.

PART I.

By C. AUER v. WELSBACH.

WHEN more than twenty years ago I discontinued my researches on the earths of gadolinite from Ytterby, I was convinced that the investigation of the earths of the ytterbium group would lead to conclusive results only when the experiments were performed on a large scale.

I hoped to further this branch of chemical research by the results of my labours undertaken from a technical point of view. The most valuable raw material was coming into the market in quantities which were increasing from year to year. But the increase of scientific knowledge was not keeping pace with this abundance of material, and although many chemists were devoting themselves to this subject, comprehensive and fundamental work was still not often to be met with.

So about six years ago I decided with proper equipment again to take up researches on the earths of the ytterbium group.

After a year's work, from many observations I was enabled to draw the conclusion that almost all the elements of the ytterbium group, as they have been hitherto described by chemists, are complex substances, and that the isolation of the actual elements is within the limits of possibility.

Thus a definite, if distant, goal was put before my experiments. I have not yet reached it; for some of the new elements have so far obstinately resisted preparation in the pure state. Thus this is the case with one of the holmium elements, which must form colourless salts, as well as with the element dysprosium, which is chemically most closely allied to it. But there can be hardly any doubt that ultimately these substances will be prepared in the pure state, and that it is only a question of time.

The final results of these experiments I shall publish in a series of separate articles, as they seem to me to offer general interest.

In the following pages I shall describe the preliminary researches as well as the process of separation, as far as they relate to the preparation of salts of ytterbium, erbium, holmium, and dysprosium.

The Working up of the Raw Material.

The raw material consisted of half a ton of raw ytterbium oxalate, which had been prepared from monazite by the Austrian Incandescent Gas Company.

It contained a fair amount of cerite earths, a tolerably large quantity of thorium, and some phosphoric acid.

As in my earlier articles I have repeatedly described the working up of the raw earths I shall now call attention only to the most important parts of the separation process.

The slightly damp oxalates were spread out in thin layers in shallow iron vessels, and then heated to a red heat with free access of air in a large muffle. The oxides, which contained carbonate, were dissolved in nitric acid. The oxides containing much carbonate were made into a paste with water, and were then added to the clear slightly acid nitrate solution in corresponding quantities in order to separate the cerium and thorium, and the whole digested for a long time on the water-bath. The precipitate formed was washed with water, dissolved in excess of hot nitric acid, and ammonium nitrate was added. After cooling, a red cerium ammonium nitrate, containing a little thorium, crystallised out. By concentrating the liquor more cerium salt could be obtained, until finally at high concentrations yellow thorium-cerium-ammonium nitrate separated out.

The mother-liquor of the thorium-cerium salts, after being much diluted with water, was precipitated with oxalic acid, and the oxalates treated as above.

This process was repeated a few times. The meta salts which separated contained no scandium, as a subsequent examination showed.

From the liquors drawn off the meta salts, which were almost free from cerium, thorium, iron, uranium, &c., I

separated directly, without warming, the ytterbium elements as basic nitric acid salts by the oxide process.

This was quite easy as long as the solution was of the right concentration and the oxides added were sufficiently finely divided.

To carry out this process, which enables large quantities of liquor to be worked up without great trouble, the oxides made into a paste with water are added by degrees to the nitrate solution and the whole allowed to stand until the decomposition of the oxides is quite finished; at the most this takes only a few hours. The basic nitric acid salts formed readily settle as a faintly pink precipitate. They are collected on a filter, and washed under pressure with water containing a small percentage of nitric acid.

After repeating this process five or six times the mother-liquor contained only a little erbium. It was put aside. Then one half of the basic nitric acid salts separated by the first precipitation was converted into nitrate by treating with water and allowing the whole to stand until the formation of the perbasic salts was ended. By cautiously adding nitric acid a clear nitrate solution free from acid was easily obtained in the cold.

From this solution the other half of the basic nitric acid salts was re-crystallised.

Using the mother-liquor of the first fraction the second was worked up similarly, and so on, till the final mother-liquor showed only a faint erbium spectrum. This liquor was again set aside. Thus the first series of the basic nitric acid salts was formed.

In the mother-liquor of the following series the amount of erbium steadily increased. For example, the mother-liquor of the tenth series had a deep pink colour owing to the large amount of erbium it contained.

In order to get the erbium fraction as free as possible from yttrium, the separation process was continued up to the twenty-first series. The fractions of this last series were not further separated from one another.

The first were a purer pink and were richer in ytterbium than the last. The essential constituents, besides erbium, were ytterbium, holmium, and dysprosium. The total weight was about 30 kilogrms.

For the further separation of these substances I employed a new method which I shall now describe in outline.

The Method of Separation.

The earths of the ytterbium group as oxalates form double salts with ammonium oxalate, of which the richest in ammonium oxalate is soluble without dissociation in a saturated solution of ammonium oxalate. The salts of the different earths exhibit considerable differences in solubility; for instance, ytterbium ammonium oxalate is more than ten times as soluble as the corresponding holmium salt. As the temperature rises the solubility of this double salt increases to a remarkable extent, as long as the ammonium oxalate solution is saturated with ammonium oxalate. When these solutions are cooled it may be seen that the more soluble salts show the phenomenon of supersaturation to a much higher degree than the less soluble.

If now a mixture of the pure ytterbium oxalates is dissolved in boiling concentrated slightly ammoniacal ammonium oxalate solution, and the solution is allowed to cool slowly, certain precautions being observed, a series of fractions is readily obtained, which differ very much from one another; while the first fraction is very rich in holmium, the last, the mother-liquor, contains besides a little erbium only large quantities of ytterbium, and thus is free from holmium. In the solution of the more soluble double salts the less soluble salts are either insoluble or dissolve only with difficulty.

These and similar observations induced me to investigate further the behaviour of these double salts under different experimental conditions. From these experiments I found that a new method of separation for the ytterbium elements could be based upon the fractional crystallisation of the ammonium double oxalates, a method which, if it offered technically many difficulties, nevertheless would be better and more convenient than any process ordinarily employed.

After I had settled all the details of the process by working up a small quantity of pure ytterbium oxalate amounting to only a few hundred grms., I proceeded to a repetition of the method on a large scale.

At this point I must remark that the sodium double salts behave like the ammonium salts, but that they are not suitable for separating the earths, chiefly on account of the difficulty of dissolving them. The potassium salts, on the other hand, behave quite differently. They are usually so soluble and crystallise so well that the separation effected by the process is very trifling under similar experimental conditions.

Details of the Separation Process.

The basic nitric acid salts, the preparation of which I have described above, contained a small amount of meta-salt which had accumulated more especially in the first fractions. To separate these compounds the basic nitric acid salts were digested continuously with water, concentrated nitric acid gradually added to the cooled mixture of perbasic salts and nitrates, until the perbasic salts were almost entirely dissolved; the fairly concentrated turbid nitrate solution was then filtered.

The clear solution was acidified, and after being greatly diluted with water was precipitated with warm saturated ammonium oxalate solution. The oxalate precipitates containing ammonium oxalate, which generally form fine precipitates yielding no concretions, were filtered and washed.

The separation process is carried out as follows:—The wet oxalate precipitates are made into a uniform thin paste with water. As much of this paste as will dissolve quickly and easily is introduced into a boiling concentrated ammonium oxalate solution containing a little free ammonia, meanwhile stirring continuously. If this limit is exceeded, and thus a persistent turbidity is produced in the solution, some solid ammonium oxalate must be added as quickly as possible in order to cause the disappearance of the turbidity. For the precipitates which result owing to a deficiency of ammonium oxalate dissolve again only with great difficulty on boiling for a long time and in presence of a large excess of ammonium oxalate.

The clear beautiful pink solution of the ammonium double oxalates is now slowly diluted while still hot with three times its volume of water or cold saturated ammonium oxalate solution, meanwhile steadily stirring. If any turbidity should result some hot saturated ammonium oxalate solution is added. The solution is then introduced into a previously warmed large porcelain dish, preferably hemispherical in shape, covered with a glass lid, and the liquor allowed to stand on the water-bath, or, better, in a thermostat at about 70° C.

The richer the solution is in dysprosium and holmium the hotter and more concentrated it must be kept. After a few hours the separation of the double salts rich in dysprosium and holmium begins with the crystallisation of the ammonium oxalate.

After twenty-four hours the mother-liquor is drawn off, the same precautions being observed as before, and the crystalline crust forming in the dish is allowed to slide off by inclining the dish.

The mother-liquor is returned to the thermostat and the temperature regulated to about 50° C. This process of allowing to stand in the the thermostat, the temperature being gradually lowered, is repeated four or five times. The last mother-liquor is allowed to stand for several days in the cold.

Thus, seven or eight crystal fractions are obtained which show striking differences among themselves. While the first is more yellowish red, the middle ones are pure pink and the last pale pink, while the mother-liquor is almost colourless after standing for some time.

The fractions are now dissolved, if necessary with the

addition of ammonium oxalate, by boiling in as little water as possible, again diluted, and fractionated as above. Then similar fractions are put together, again dissolved, and the process continued, the mother-liquor of the preceding fraction being always used to dissolve each fraction.

The arrangement of the fractions into series is performed according to the spectra of the crystals and not according to the spectra of the liquors, because the crystalline ammonium double oxalates of holmium and erbium have very marked spectra, while those of the fairly dilute solutions, on the contrary, are not sharp. A direct vision spectroscope is used with a very narrow slit, and it is best to work in sunlight or in light from an arc lamp. For those who are not skilled the former is to be recommended, because the Fraünhofer lines greatly assist the identification.

The dispersion and magnifying power of the instrument must be great enough for the D-lines to appear distinctly double. I used for these observations a Browning's direct vision spectroscope, with a slit which could be altered from the side.

From the intensity of the lines shown in a crystal spectrum it is usually fairly easy for a worker who has had experience of the method to draw definite conclusions as to the mother-liquor.

Nevertheless, small errors may be made, but they do not natter much. If, moreover, the worker has been making these observations for some time, the eye gets so keen in observing slight differences of shade that it is generally sufficient to observe the colour of the fractions in diffuse daylight in order to be able to deduce their positions in the series.

After several series the first fractions become paler, and the holmium and dysprosium lines appear more clearly; in the final members, on the other hand, the holmium line $\lambda = 535$ gradually disappears. The fractions become more and more pink in colour. Soon the characteristic spectrum of pure erbium appears.

As the separation is continued in the first fractions the erbium line $\lambda = 540$ in the green, disappears, and their colour becomes light orange-yellow. The difficulty in dissolving them becomes greater and greater, and in order to effect complete solution ammonium oxalate must often be added to the boiling mixture. The fractions containing erbium, at the end of the series, continually get paler. The absorption spectrum gradually changes; the characteristic line in the green disappears by degrees, and a new erbium spectrum, which I shall call "spectrum erbium γ_1" becomes more and more distinct.

After repeated evaporation the final mother-liquors are colourless. With further fractionation colourless crystal aggregates separate out from it; they contain a large excess of ammonium oxalate.

The liquors are now allowed to stand for a long time in the cold; once more precipitates rich in ytterbium separate out. As soon as the first and last members of the long series become small in quantity they are put back until after several repetitions of the crystallisation process—after many series, as I shall call it for the future—homogeneous products are obtained. The similar fractions are then put together and joined to the series as the extreme members.

In the above outlined description I think I have explained the nature of the separation process as far as it is of scientific interest, and will not therefore give a complete description of the lengthy separation processes themselves, which would only be tedious. I shall merely call special attention to some points which are of importance in the carrying out of the process. The first working up naturally takes place in many parallel series. As the series contained far more erbium than was necessary for the scientific investigation of this substance a large part of the erbium fractions containing a little holmium were put back at the beginning. All fractions were finally united in one chief series. After about forty series the first members of the chief series showed no holmium spectrum; they were put aside. I soon added others to them, and afterwards I regularly excluded each first crystalline fraction from the process. Thus gradually a long series of fractions was formed, which were all more or less different from one another. In addition there were the final mother-liquors put aside from the series, which had been put together every ten series. They were again fractionated systematically, and the fractions obtained added to the others.

The number of fractions had then risen to about one hundred. Together they made an unusually instructive picture. The first fractions put aside were almost white, the following up to about the fifteenth were pale yellow, then they became orange-yellow, while towards the middle they became more and more pink. After the beautiful pink erbium fractions came pale pink fractions, till finally towards the end of the series came the colourless ytterbium salts.

Observed directly in transmitted light the first crystal fractions showed a somewhat altered dysprosium spectrum, besides traces of the spectrum of neodymium. The pale yellow ones gave the normal dysprosium spectrum, the pure orange the holmium spectrum, while the most intensely pink coloured fractions exhibited only the characteristic erbium spectrum.

As the pink colour got paler the erbium spectrum altered, and gradually passed into the spectrum of Er γ. Thenceforward the bands of thulium steadily increased in strength until they reached their greatest intensity in the fractions which were only faintly pink. In the nearly colourless fractions they got fainter and fainter again, not disappearing altogether, however, until the completely colourless ytterbium fractions were reached.

Similar although not such marked differences were exhibited by the nitrate solutions.

The visual examination of the spark spectra led to important results. In the first fractions, which possessed an exceedingly complicated spectrum, lines could be seen which did not appear to coincide with the lines of known elements. The pale yellow and yellow fractions gave a more or less pure spectrum of ordinary holmium, while the orange-yellow, *i.e.*, just those which showed the most intense and purest absorption spectrum of holmium, did not exhibit the characteristic lines of holmium in addition to a usually bright yttrium spectrum; other groups, however, which were very rich in lines, appeared. Among other effects their prevalence made the somewhat pale yttrium spectrum appear as if on a light ground.

In the more decidedly pink-coloured fractions the yttrium spectrum again disappeared. The intensely pink-coloured fractions gave the spark spectrum of erbium. As the fractions got paler the spectrum of ytterbium began to appear more clearly until it reached its full brightness in the colourless fractions.

Important results were also obtained from the thorough investigation of the final mother-liquors, which naturally contained the most easily soluble parts of the double oxalates. The first of these liquors, which I examined at the beginning of the separation process, contained thorium as meta-salt, also some uranium and iron as well as other substances, which had originated partly from the large quantities of water used and partly from the ammonium oxalate; amongst them were aluminium hydroxide, silicic acid, alkalis, &c.; of the rare earths only some ytterbium and a minute quantity of scandium could be detected.

The other final mother-liquors I also subjected to a careful examination. After diluting them with water, nitric acid was carefully added until all the oxalates of the earths had been separated. The liquid filtered off from the oxalates was evaporated and the residue ignited. The residue left after ignition contained, besides much silicic acid and aluminium hydroxide, a small amount of platinum metals and elements allied to tin, as well as a very small quantity of rare earths. I added the last, after I had again converted them into oxalates, to the oxalate precipitate first obtained. These oxalates also contained some thorium, but curiously enough no scandium. After the thorium had been separated I again dissolved the oxalates of the earths in ammoniacal ammonium oxalate solution,

filtered from the undissolved silicic acid and fractionated the solution carefully until a small residue was obtained. This should now contain the purest ytterbium. But this conclusion was contradicted by the spectral examination; for the spark spectrum, which was free from the lines of foreign bodies, showed, when compared with the ordinary ytterbium spectrum, most striking differences. These differences are the first definite indications of the decomposability of ytterbium.

I have omitted to give representations of the different spectra with this article because I shall go more fully into all the characteristic spectra in the special articles mentioned previously.—*Monatshefte für Chemie*, xxvii., No. 8, 935.

A STUDY OF THE METHODS FOR THE DETERMINATION OF ESTERS, ALDEHYDES, AND FURFURAL IN WHISKY.*

By L. M. TOLMAN and T. C. TRESCOT.

(Concluded from p. 185).

Determination of Aldehydes.
By L. M. Tolman.

The method for the determination of aldehydes as provisionally adopted by the Association was found to be entirely unreliable—and, in fact, the reagents as given were not correct, as they reacted with alcohol free from aldehydes. The reason for this was that there was not enough sulphur dioxide in the solution. The amount of sulphur dioxide in the solution greatly affects its sensitiveness, and the main point to be determined was how to prepare a solution that would not react with pure alcohol and was still sensitive enough. By experimenting with a number of mixtures, it was found that a reagent that contained 5 grms. of sulphur dioxide to the litre gave only the slightest tinge of colour with the pure alcohol and was sensitive to 0·0001 grm. of aldehyde in 50 cc. From this it can be seen that it is very necessary that the amount of sulphur dioxide present should be accurately determined, and that the use of a solution of sodium bisulphite of a definite specific gravity is not to be relied on in preparing this reagent. If the sulphite is to be used, its strength in sulphurous acid should be determined by use of a standard solution of iodine. Another objection to the Association method was the fact that the test is made in a 30 per cent alcohol solution. The objection to using this strength of alcohol is that when most pure whiskies are diluted to this alcoholic strength they are turbid, and this turbidity greatly interferes with the reading of the amount of aldehydes in the colorimeter. The following are the reagents and method finally adopted for our work.

Reagents.

1. *Alcohol Free from Aldehydes.*—This is prepared by first re-distilling the ordinary 95 per cent by volume alcohol over caustic soda or potash and then adding 2 to 3 grms. per litre of *m*-phenylenediamine hydrochloride, and digesting at ordinary temperature for several days or with an upright condenser on the steam-bath for several hours and then distilling slowly, rejecting the first 100 cc. and the last 200 cc.

2. *Sulphite-fuchsin Solution.*—Take 0·500 grm. of pure fuchsin and dissolve in 500 cc. of water; then add 5 grms. of sulphur dioxide dissolved in water, make up to a litre, and allow to stand until colourless.

This solution should be made up in small quantities, as it retains its strength for only a very few days.

3. *Standard Acetic Aldehyde Solution.*—Prepared as directed in Vasey ("Analysis of Potable Spirits," p. 30).

Aldehyde ammonia is taken as the starting-point. Grind this in a mortar with ether and decant the ether, repeating the operation several times, then dry the purified substance in a current of air and finally in a vacuum over sulphuric acid. Dissolve 1·386 grms. of this purified aldehyde ammonia in 50 cc. of 95 per cent by volume alcohol; to this add 22·7 cc. of normal alcoholic sulphuric acid, and then make up to 100 cc. and add 0·8 cc. to compensate for the volume of the ammonium sulphate precipitate. Allow this to stand over night and filter. This solution contains 1 grm. of acetic aldehyde in 100 cc. and will retain its strength.

The standard found most convenient was 2 cc. of this strong aldehyde solution diluted to 100 cc. with 50 per cent by volume alcohol. One cc. of this solution is equal to 0·0002 grm. of acetic aldehyde. This solution should be made up fresh every day or so as it loses its strength.

The method of determining aldehyde is as follows:—Five or ten cc. of the distillate as prepared for the determination of esters are placed in one of the colorimeter tubes and made up to 50 cc. with aldehyde-free alcohol (strength 50 per cent by volume) placed in a water-bath kept at 15° until it reaches the temperature of the bath; then 25 cc. of the sulphite-fuchsin solution, which is also at 15°, is added. The two solutions are thoroughly mixed and allowed to stand in the bath held at 15° for fifteen minutes, and then compared in the colorimeter with standard aldehyde solutions.

Standards containing 0·0005, 0·0010, and 0·0015 grm. of acetic aldehyde are prepared at the same time and under the same conditions. The standard which matches the sample nearest is used for comparison in the colorimeter. If the colour of the sample is stronger than any of the standards, less of the sample must be taken, as colours deeper than that produced by 0·0015 grm. of acetic aldehyde cannot be compared with accuracy.

The regulation of the temperature at which the test is made is of the greatest importance, as the accuracy of the method is entirely dependent on the temperature being held constant at about 15° during the reaction. If this is not done, the colour developed in the blank which should be run with every determination will be so strong as to interfere with the method. In fact, it is impossible to do anything with the method quantitatively without controlling the temperature exactly.

The comparisons in the colorimeter must be made as quickly as possible, as the colour rapidly deepens if the room temperature is much above 15°. The standard aldehyde solution may be checked against the colour glasses of the Lovibond tintometer. In our work, following the exact conditions given above, red No. 5 and blue No. 1·25 combined gave the colour developed by 0·0005 grm. of acetic aldehyde in 50 cc., looking through 42 mm. depth of solution. This, however, should not be taken as a standard, but each analyst should compare his reagents under the conditions under which he is working with the standard glasses. This will be found to be a valuable check on the solutions.

The amount of colour developed by acetic aldehyde under these conditions is not in direct proportion to the percentage of aldehyde present. A standard containing 0·001 grm. develops about three times as much colour as a standard 0·0005 grm. and about one-half the colour of a standard containing 0·0015 grm. This necessitated the preparation of a number of curves, from which Table V. was prepared.

This table is used in the following manner:—The colorimeter tube containing the standard solution is placed in the colorimeter at a definite reading, say at 25. The tube containing the sample is now placed in the instrument and compared with the standard by moving it up and down until the colours match, which is at, say, 19. Now suppose the standard contained 0·0005 grm. of aldehyde and was set in the instrument at a reading of 25, then look in the column under the 0·0005 grm. reading 25 until you come to the place opposite the reading of the sample and

* From the *Journal of the American Chemical Society*, xxviii., No. 11.

TABLE V.—*Calculation of Aldehydes from Colorimeter Readings.*

Sample reading.	0·0005 grm. standard. Reading 15.	0·0005 grm. standard. Reading 25.	0·0010 grm. standard. Reading 10.	0·0010 grm. standard. Reading 20.	0·0015 grm. standard. Reading 10.
	Mgrm.	Mgrm.	Mgrm.	Mgrms.	Mgrms.
10.		0·80	1·00	1·50	1·50
11.		0·76	0·94	1·40	1·40
12.		0·72	0·89	1·30	1·30
13.		0·69	0·83	1·25	1·25
14.		0·67	0·79	1·20	1·20
15.	0·50	0·65	0·76	1·15	1·15
16.	0·48	0·62	0·73	1·10	1·10
17.	0·465	0·60	0·70	1·08	1·06
18.	0·45	0·59	0·685	1·05	1·03
19.	0·43	0·575	0·67	1·03	1·00
20.	0·415	0·56	0·655	1·00	0·97
21.	0·40	0·55	0·64		
22.	0·38	0·54	0·62		
23.	0·365	0·525	0·61		
24.	0·35	0·515	0·59		
25.	0·33	0·50	0·58		
26.	0·315		0·565		
27.	0·30		0·55		
28.	0·29		0·535		
29.	0·28		0·52		
30.	0·27		0·50		
31.	0·265		0·49		
32.	0·255		0·485		
33.	0·245		0·48		
34.	0·235		0·47		
35.	0·23		0·465		
36.	0·22		0·46		
37.	0·21		0·455		
38.	0·20		0·45		
39.	0·195		0·445		
40.	0·19		0·44		
41.	0·185		0·435		
42.	0·18		0·43		
43.	0·175		0·425		
44.	0·17		0·415		
45.	0·165		0·41		
46.	0·16		0·405		
47.	0·155		0·40		
48.	0·15				
49.	0·145				
50.	0·14				

there find the milligrms. of aldehyde, which, in this case, is 0·575. The colorimeter used in this work was that described by Schreiner (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1192—1203), and it was found to be very satisfactory and convenient, being preferred in this work to the Soleil-Dubosq instrument, as it gives a much wider range of comparison. Schidrowitz (*Journ. Soc. Chem. Ind.*, 1902, xxi., 814—819) does not use the distillate for this determination but clarifies the whisky with basic lead acetate, colours his standard slightly with tincture of galls to match the colour of the decolorised whisky, and then treats with the reagent; but this method, while it is applicable to pure whiskies light in colour, cannot be applied to whiskies that are coloured with caramel, as caramel is not removed by lead acetate. Hence, in order to obtain comparable results, it is necessary to work on the distillates in all whiskies.

The claim that aldehydes are formed in the distillation is not substantiated by our experiments on 150 samples of new brandies in which the determination of aldehydes was made on the original sample and on the distillate. The average on the original was 172 mgrms. per litre, while the average on the distillate was 173 mgrms. per litre. These results show several things. First, that the method gives comparable results and results that can be duplicated, as in this work the determination on the original was made on one day and the determination on the distillate the next day. Second, that there is no loss or gain in aldehydes by distillation. Third, that it is an exact method, as is shown by the close agreement of results.

DETERMINATION OF FURFURAL.
By L. M. TOLMAN.

Schidrowitz does not use the distillate for this determination, but follows the same procedure in the determination of furfural as in the determination of aldehydes. The same objection holds in this method, however, as in the aldehyde determination, namely, that the method cannot be applied to all the whiskies on account of the impossibility of removing caramel when present, so that it is better to use the distillate in all cases.

The following are the reagents and the method used for the determination of furfural:—Colourless aniline, hydrochloric acid (sp. gr. 1·125), alcohol free from furfural. The aniline was obtained by re-distilling the ordinary dark coloured aniline. This must be kept in the dark or it will soon become coloured. The ordinary 95 per cent by volume alcohol re-distilled over caustic soda or alkali is practically free from furfural.

Standard Furfural Solution.—Prepare the standard furfural solution by weighing 1 grm. of re-distilled furfural and dissolving it in 100 cc. of 95 per cent by volume alcohol. This strong solution will keep. Standards for use are made by diluting 1 cc. of this solution to 100 cc. with 50 per cent by volume alcohol. One cc. of this solution contains 0·0001 grm. of furfural.

The method for determining furfural is as follows:—Ten or 15 cc. of the distillate as prepared for the determination of esters is placed in a colorimeter tube and diluted to 50 cc. with 50 per cent by volume alcohol free from furfural. The tube is placed in a water-bath kept at 15°, and allowed to remain until it reaches the temperature of the bath. Then 2 cc. of the aniline and 0·5 cc. of the hydrochloric acid are added, and the whole thoroughly mixed. The tubes are left for fifteen minutes in the bath at 15°, and then taken out and read in the colorimeter against standard furfural solutions.

Standards containing 0·0001, 0·0002, and 0·0003 grm. of furfural are prepared and treated in the same manner. The standard which matches nearest the colour in the sample is used for comparison in the colorimeter.

The amount of colour developed by the furfural solutions is in direct proportion to the amount of furfural present, so that calculations can be made directly from the readings.

The temperature greatly affects the reaction, and it should be carefully regulated.

Hydrochloric acid was used instead of acetic acid on account of the fact that the acetic acid available gave a very decided colour reaction, which interfered with the test. Another advantage of hydrochloric acid is that it is more uniform in quality than acetic acid, and in these colour tests it is necessary that the conditions shall remain constant in order to obtain comparable results. The occurrence of furfural in acetic acid or some substance that gives a similar colour reaction with this reagent seems to be quite common, as it has been noted by a number of observers. The substance that gives the test can be destroyed by heating the mixed reagent, but this interferes with its sensitiveness.

In order to settle the question whether all the furfural will be found in the distillate, and also whether there is any formation of furfural in distillation, the determination was made on a number of samples of slightly coloured and colourless spirits, in the original and in the distillate.

The results on 120 samples gave an average of 23·4 mgrms. per litre on the original and of 23·2 mgrms. per litre on the distillate. This shows that there is no loss or gain of furfural by distillation; it also shows that the method is reliable, as the same conditions held in these determinations as in the work on aldehydes.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part II.—Analysis of the Silver, Copper, and Tin Groups.

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 187).

Procedures and Notes.

Analysis of the Silver Group.

Procedure 11.—To the cold aqueous solution of the substance (P. 3) add 4 cc. HCl (1·12) from a small graduate. (White precipitate, presence of *silver group*). Filter, and wash the precipitate with a small quantity of cold water, adding the washings to the filtrate until its volume is about 40 cc. (Precipitate, P. 12; filtrate, P. 21).

Notes.

1. Non-formation of a precipitate proves absence of silver and mercurous mercury, but not of lead (or thallous thallium), since $PbCl_2$ (and TlCl) are fairly soluble in water. Owing to the common-ion effect, the solubility of the chlorides is greatly decreased by the addition of HCl; but 20 to 40 mgrms. Pb (and 5 to 15 mgrms. Tl) may remain in solution, and thus escape detection in this group.

2. Since the subsequent precipitation of the copper and tin groups by H_2S must be made in a dilute HCl solution of known strength, a definite amount of HCl is added at this point, and the solution is diluted to a known volume.

3. The addition of the first few drops of HCl may cause the precipitation of the white oxychlorides BiOCl and SbOCl; but these precipitates dissolve when the rest of the acid is added. If, however, the solution were largely diluted with water, the precipitate might again separate.

4. From an alkaline solution HCl might precipitate many other substances, as described in P. 3, N. 4. Such a solution is therefore first treated with HNO_3 (P. 3).

Procedure 12.—Pour repeatedly through the filter containing the HCl precipitate (P. 11) a portion of 10 to 20 cc. boiling water. Wash the residue thoroughly with hot water. (Residue, P. 15; solution, P. 13).

Procedure 13.—Add to the aqueous extract from the HCl precipitate (P. 12) one-fifth its volume of concentrated H_2SO_4; cool, shake the mixture, and allow it to stand for five minutes. (White precipitate, presence of *lead*). Filter, wash the precipitate with H_2SO_4 (1·20), and then with a little water. (Precipitate, P. 14; filtrate, reject or test for thallium by *P. 13a).

Note.

1. $PbSO_4$ is slightly soluble in water, but, owing to the common-ion effect, much less so in dilute H_2SO_4; hence, H_2SO_4 is added in excess to the solution and to the wash-water.

**Procedure* 13a.—To test for thallium add to the filtrate from the H_2SO_4 precipitate (P. 13) 2 to 3 cc. KI solution. (Yellow precipitate, presence of *thallium*). If the solution becomes brown, owing to the liberation of free iodine, add a little H_2SO_3 solution.

**Notes.*

1. Thallous iodide is much less soluble than the corresponding chloride, and its solubility is greatly decreased by KI, owing to the common-ion effect. PbI_2 is also difficultly soluble, but cannot be precipitated here, since lead has been removed by H_2SO_4 in P. 13. The presence of even 0·5 mgrm. thallous thallium in 15 cc. of solution may easily be detected in the cold by means of KI. Free iodine oxidises thallous to thallic salts, but these, as well as the iodine itself, are reduced by H_2SO_3.

2. Thallous salts are oxidised to thallic salts rapidly by halogens and *aqua regia*, and slowly by hot concentrated HNO_3. Upon evaporating a thallic chloride ($TlCl_3$) solution and heating the residue at 120°, more or less complete reduction takes place by decomposition into TlCl and Cl_2. Pure thallic salts give no precipitate with HCl, thallous salts a white one; while mixtures of them give yellow precipitates ($TlCl_3.xTlCl$). For these reasons, even when the substance has been dissolved in HNO_3, and the solution has been evaporated as described in P. 4, thallium will be precipitated with this group by HC. if much of it is present.

Procedure 14.—Pour repeatedly through the filter containing the H_2SO_4 precipitate (P. 13) a 10 to 20 cc. portion of a 10 per cent ammonium acetate solution; add to the filtrate a few drops K_2CrO_4 solution and 2 to 5 cc. dilute acetic acid. (Yellow precipitate, presence of *lead*).

Notes.

1. The solubility of $PbSO_4$ in solution of ammonium acetate ($NH_4C_2H_3O_2$) depends on the formation by metathesis of undissociated lead acetate, which is much less ionised than most other salts of the same type. On the addition of a chromate to this solution the much more difficultly soluble $PbCrO_4$ is precipitated, and is not dissolved by dilute acetic acid.

2. This confirmatory test is also applied to the $PbSO_4$ precipitate obtained in the analysis of the copper group (P. 26). In that case the precipitate may also contain bismuth, which would dissolve in ammonium acetate, and give a yellow precipitate on the addition of K_2CrO_4; but this precipitate, unlike the $PbCrO_4$, dissolves readily in acetic acid.

Procedure 15.—Pour repeatedly through the filter containing the residue insoluble in hot water (P. 12) a 10 to 20 cc. portion of NH_4OH (0·96). (Black residue on the filter, presence of *mercurous mercury*). Acidify the filtrate with HNO_3. (White precipitate, presence of *silver*).

Notes.

1. The black residue produced by the action ot NH_4OH on Hg_2Cl_2 is a mixture of finely divided mercury with the white mercuric compound $HgClNH_2$. The reaction is expressed by the equation $Hg_2Cl_2 + 2NH_4OH = HgClNH_2 + Hg + NH_4Cl + 2H_2O$. The compound $HgClNH_2$ may be considered to be a derivative of $HgCl_2$, formed by replacing an equivalent of chlorine by the univalent radical NH_2.

2. It is to be noted that mercury will not be in the mercurous state, and therefore will not be precipitated with this group, if the substance has been heated with strong nitric acid or aqua regia.

3. AgCl dissolves readily in NH_4OH, owing to the formation of a soluble complex salt, $Ag(NH_3)_2Cl$, which in solution is largely dissociated into $Ag(NH_3)_2^+$ and Cl^- ions. This complex cation has so slight a tendency to dissociate that in a normal solution of NH_4OH the ratio of its concentration to that of the simple Ag^+ ion is about 10^7.

4. HNO_3 re-precipitates the AgCl from its solution in NH_4OH, owing to the facts that the complex cation is slightly dissociated according to the equation $Ag(NH_3)_2^+ = Ag^+ + 2NH_3$, and that the NH_3 combines with the added acid, forming NH_4NO_3, thus causing the complex cation to dissociate further, until the Ag^+ concentration increases to such an extent as to make the product of it into the Cl^- concentration greater than the solubility product for AgCl.

5. The test is less delicate when the NH_4OH_3 is neutralised with HCl, owing to the solubility of AgCl in strong chloride solutions, which arises, probably, from the formation of a salt with a complex anion, like $NH_4^+AgCl_2^-$.

(To be continued).

* From the *Technology Quarterly*, xix., No. 3 September, 1906.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 22nd, 1907.

Prof. J. PERRY, F.R.S., President, in the Chair.

A PAPER by Mr. POCHIN on "*Experimental Mathematics*" was read by the author.

An instrument for describing logarithmic spirals was exhibited, and it was shown how the principal properties of logarithms and of the equiangular spiral may be established as experimental results. A spiral was described with an angle of 45°, and the positions of the radius vector, representing the first ten natural numbers, were drawn in. Cardboard sectors having been cut to fit the various angles, under the successive positions of the radius vector, it was shown that these sectors represented the logarithms of the numbers. Multiplication and division were illustrated by placing the sectors in juxtaposition, so that the angles were added or subtracted, the result being read off directly from the curve. A table of natural logarithms was also prepared from the spiral, by direct measurement with a foot-rule and a protractor graduated in radians. A geometrical analysis was given, confirming the accuracy of the experimental results, and affording an independent proof of the exponential theorem. A second spiral was drawn with an angle $\tan^{-1} M$, thus giving common logs. in terms of the radian; and it was shown that, by using a suitably-graduated protractor or modulus, one system transformed into the other. A Boucher's Circle and a slide-rule were also derived practically from the spiral. The differentials $d \log_e r/dr$ and $d \log_{10} r/dr$ were shown graphically, as well as the properties of the evolute and involute. The paper was put forward as an attempt to show how pure mathematics may be taught experimentally, and in the belief that many boys derive benefit from an alternative treatment which enables them to employ the sense of touch in addition to those of sight and hearing.

Mr. W. A. PRICE expressed his interest in the paper and described an instrument, constructed somewhat on the lines of that described by the author, which could be used to draw the exponential curve $y = ae^{x/b}$. He pointed out that any exponential law was a relation between two quantities changing in arithmetical and geometrical progression respectively. In an exponential curve in which the ordinates change in G.P. and the abscissæ in A.P., the formation of the logarithmic scale can be shown by marking on the scale of abscissæ the corresponding values of the ordinates. Logarithms should form part of the subject of arithmetical and geometrical progressions; the conception of continuous growth being added by interpolation of terms in the usual series.

The CHAIRMAN said the paper was interesting to those acquainted with logarithms and logarithmic spirals, but in his opinion the methods described by the author were not the best for beginners. He pointed out that the early geometers used practical methods to check the results of their theoretical reasoning.

A paper entitled "*Logarithmic Lazy-tongs and Lattice-works*" was read by Mr. T. H. BLAKESLEY.

If two straight rods, AB, CD, are jointed at E, and so related that the extremities ACBD lie in the circumference of a circle, they will fulfil this condition when the angle between them is changed.

Suppose that AE is taken as unity, and that $ED = n$, $EC = m$, m and n being quite independent. Then $EB = mn$ as a consequence.

If another pair of rods, DF, BG, similar to the first pair but bearing the ratio $n : 1$ to it, be jointed at D and B to the first pair, and to the extremities FG of this pair a third pair be again jointed, and a fourth to this, and so on, the ratio of each pair to the preceding one being $n : 1$, the resulting linkage is called by the author a Logarithmic Lazy-tongs.

The points ADG . . . . lie upon an equiangular spiral, whose characteristic angle α is given by the equation—

$$\tan \alpha = \frac{\text{ECA} - \text{EAC}}{\log n}.$$

By opening or shutting the angles at E, the numerator of the expression on the right is varied, but its denominator remains constant. It follows that the characteristic angle of the spiral (α) may be varied at pleasure, by causing the angles at E to change.

A lazy-tongs constructed as above is said to be in the n direction. It is clear that any of the four sides, AC, CB, BD, AD, might be chosen as that to which the next pair of rods is to be attached, care being taken to make the ratio correspond to the direction chosen.

If CB is chosen the ratio must be $m : 1$, and a lazy-tongs in the direction m will result, the angular shift at each step being EAD − EDA.

Suppose pairs added in the m direction to both CB and BF; then it is easy to see that these two pairs will have, in addition to B, another common point, viz., that which is homologous to B in the m direction. In fact the same pair is arrived at whether by moving once in the n direction and then once in the m direction, or *vice versâ*. It is clear that a joint may be added at the common point, and that the rule is a general one, and that all plane space may be occupied by such a linkage, which is called a Logarithmic Lattice-work. Such a lattice-work moves so that the angles at E, and points homologous, will remain equal.

An equiangular spiral also passes through AB, and points homologous in the mn direction. Its characteristic angle α is such that—

$$\tan \alpha = \frac{\text{BCA} - \text{ADB}}{\log mn}.$$

Circles and straight lines, being limiting cases of equiangular spirals, will therefore occur with some arrangements. For instance, if $mn = 1$, the curves in the mn direction are circles.

If the n curves are circles, by n being made equal to unity, the angle EAD is equal to EDA; and the difference between these angles being then zero, there will be no angular shift in the m direction, and the m curves will therefore be straight lines.

The author indicated how, by controlling the three variables mn and the angles at E, a geometrical solution of such problems as occur in cables subject to alternating currents may be reached.

Mr. W. A. PRICE pointed out that the principle of extending a quadrilateral by constructing similar and similarly disposed figures on the sides, and thus covering an indefinite area, was not confined to inscribable quadrilaterals nor even to plane ones. A gauche quadrilateral with its diagonals is a tetrahedron, and may be regarded as contained by three pairs of opposite edges. Any two of these pairs may be used to originate a set of quadrilaterals on the author's plan, which will lie on the surface of a helicoid, and whose sides and angular points will describe helical spirals. There will be three sides each of two pairs of edges from each of which may be developed a helicoidal surface with its families of helical spirals; so that from a single gauche quadrilateral three helicoids may be developed.

Mr. R. J. P. ROBERTS exhibited a Compensated Micro-manometer, described in the *Proceedings of the Royal Society*, Sect. A, vol. lxxviii.

A paper by Mr. GARRETT on "Electrical Conduction produced by heating Salts" was postponed.

NOTICES OF BOOKS.

Introduction to Physical Chemistry. By James Walker, D.Sc., Ph.D., F.R.S. Fourth Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1907.

This introduction to physical chemistry demonstrates perhaps for the first time in the English language how profitable the study of this branch of chemistry can be made to students whose knowledge is only quite elementary, provided that sufficient care is taken to emphasise the connections between ordinary chemical knowledge and the new conceptions, and to treat the subject practically. Such being the case, it is not surprising that the book has been widely adopted in science schools and colleges, and that a new edition has been called for. In this, new data have been substituted for old when further work has shown that the latter were inaccurate, and chapters have been added on Atomic and Molecular Dimensions, and on Neutrality and Salt Hydrolysis, while some minor additions have also been made to the text. As before, general references are given to original authorities at the end of each chapter, and the book is such a good elementary text-book that those who are taking up the study of physical chemistry should not fail to get a copy; they will find that it well repays careful reading, both by the information it gives and the interest it awakens.

The World Machine. By Carl Snyder. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

The author of this book believes that possibly we have now at last come to know the cosmos as it is, regarding the universe as a cyclic process, or a ceaseless machine, without beginning or end. This marks a definite stage in men's knowledge, and calls for a historian to describe the method by which it has been attained, a task which has not yet been undertaken in that broad spirit which it demands. So, without going very deeply into the development of any branch of cosmic science, the author now sets before his readers an outlined but complete world-picture, discussing such items of knowledge as possess both finality and completeness, as distinguished from the so-called facts which lie in the debateable region, where gaps of ignorance have to be bridged by temporary hypotheses, which we know will ultimately fall, shattered by the weight of increasing knowledge. Thus the author in successive chapters describes how definite ideas were gradually reached concerning the shape of the earth, the fixity of the sun, and so forth to the last and still unanswerable riddle—gravitation—attaching to each advance the name of the moving spirit through whom it was achieved, and prefacing the whole with an interesting introduction on the overcoming of appearances and the beginnings of certitude. The author's style is particularly fanciful and imaginative, but he shows good judgment in discerning the true value of each man's work, a great merit in the writer of a history. In this book, which may be regarded as the first of a series of three, he contents himself with the recital of facts, hoping later in subsequent volumes to point the moral of the tale and discuss the mechanism of life.

The Gas Engineers' Pocket-book. By Henry O'Connor. Third Edition. London: Crosby Lockwood and Son. 1907.

This pocket-book contains tables and memoranda relating to the manufacture, distribution, and use of coal-gas, and to the construction of gas works, besides much miscellaneous information and general mathematical tables. One excellent feature is the abundance of graphic representations of numerical data, which are very convenient and clear, and gas engineers will find the book both comprehensive and concise, and, in fact, invaluable to them.

An Elementary Text-book of Metallurgy. By A. Humboldt Sexton, F.I.C., F.C.S. Fourth Edition. London: Charles Griffin and Co., Ltd. 1907.

The student who is beginning metallurgy will find in this book a course of elementary work which will exactly meet his needs. The treatment is sufficiently wide to enable him to get from it a general knowledge of metallurgy upon which to base the specialised study of the particular branch in which he is most interested, and at the same time it is by no means so slight as to be valueless. The appliances and materials employed in all common processes are first described, and the most important methods of extraction of, for instance, iron, copper, lead, &c., are then treated in detail, the chemistry of each process being very carefully explained, while plans showing the chief features of the more complicated extractions help to make them clear and to fix them on the memory. The alloys are included, and the applications of electricity to metallurgy are treated very shortly in one chapter. A course of practical work to illustrate the text is also outlined, and the book is in every respect very suitable for elementary students.

Utilisation of Nitrogen in Air by Plants. (II.). By Th. Jamieson. Aberdeen: Agricultural Research Association.

Undaunted by the reception accorded to his first work on this subject, a reception which, generally speaking, was far from favourable, the Director of the Aberdeen Agricultural Research Station, with laudable perseverance and belief in his discovery, has set about accumulating fresh evidence to confirm his theory of the direct utilisation of the nitrogen of the air by plants, and he has endeavoured to meet his opponents' genuine objections very fairly, while he has shown himself undisturbed by the animosity and even ridicule with which his criticisers have received his first announcement on the subject. He now describes quantitative experiments, and gives the details of series of tests, in which plants were grown under varying conditions and the nitrogen in them determined with every possible precaution. It was then always found that the nitrogen present in the plant after growth exceeded that provided (in the original plant and the materials used) by a considerable amount. Mr. Jamieson gives full information relating to the methods he adopted, and urges those interested to investigate the question for themselves, recommending the water fairy plant as suitable for the purpose. Clearly, the duty of repeating his experiments and detecting his error, if any, now rests with his opponents, who may not be disposed to accept his figures without confirmation, nor, we may add, be able to refute them without careful and accurate experimental work, such as Mr. Jamieson himself has evidently devoted to the study of this most important question.

Synopsis of Mineral Characters. By Ralph W. Richards. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

In this book an alphabetical list is given of the commonest minerals, together with short statements of their distinguishing characteristics. Thus, crystalline form, cleavage, hardness, &c., are all enumerated, and the synopsis will make the identification of minerals in the field a matter of comparative simplicity. Some chemical properties are added, such as the phenomena exhibited before the blow-pipe, and on heating in a closed tube, and also solubility in hydrochloric or other acid, and the author has taken pains to make the little book complete as far as it goes, although of course it will not take the place of a reference book on the identification of minerals.

MEETINGS FOR THE WEEK.

MONDAY, 29th.—Society of Arts, 8. (Cantor Lectures). "Detergents and Bleaching Agents used in Laundry Work," by Prof. Herbert Jackson, F.I.C., &c.

TUESDAY, 30th.—Royal Institution, 3. "Stimulation, Luminous and Chemical," by Prof. William Stirling, M.D., &c.

—— Society of Arts, 8. "Lustre Pottery," by William Burton.

WEDNESDAY, May 1st.—Society of Arts, 8. "The Defence of the Sea Coast from Erosion," by Alfred Edward Carey, M.Inst.C.E.

—— Royal Institution, 5. Annual Meeting.

THURSDAY, 2nd.—Royal Institution, 3. "The Bacchants of Euripides," by A. W. Verrall, Litt.D.

—— Society of Arts, 4.30. "The Applicability to India of Italian Methods of Utilising Silt." by Sir Edward C. Buck, K.C.S.I., &c.

—— Chemical, 8.30. "Chemical Action of Exradio—(1) Action on Distilled Water, (2) Action on Copper Salts in Solution," by Sir W. Ramsay. "Freezing-point Curves of the Menthyl Mandelates," by A. Findlay and E. M. Hickmans. "Constitution of Homo-eriodictyol, a Crystalline Substance from Eriodictyon Leaves," by F. B. Power and F. Tutin. "Relation between Valency and Heats of Combustion," by G. Le Bas.

FRIDAY, 3rd.—Royal Institution, 9. "Dexterity and the Bend Sinister," by Sir James Crichton-Browne, F.R.S.

SATURDAY, 4th.—Royal Institution, 3. "Scientific Work in the Sea Fisheries," by Prof. W. C. McIntosh.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2475.

ON THE

PURIFICATION AND TESTING OF SELENIUM.*

By R. THRELFALL, F.R.S.

In 1895 I was enabled by a Royal Society grant to obtain about 100 lbs. weight of selenium of about 99·5 per cent selenion content. The grant was applied for to enable me to extend to selenion the investigations already made on purified sulphur (Threlfall and Brearley, *Phil. Trans.*, A, 1896). For the purpose of the investigation it was necessary to purify the selenion beyond the standard usual for material to be used in atomic weight investigations. This proved in the event to be impossible on account of the comparatively slight volatility of selenion dioxide, and the impossibility of preventing its formation in the course of the electric measurements I proposed to carry out. Meanwhile, I had prepared a great deal of very pure selenion, and began to investigate its properties—other than those of conduction, for which absolute purity is essential (*Phil. Mag.*, Series 5, 1896, p. 42; *Phys. Review*, 1897, vols. iv. and v.).

The method of purification adopted was essentially that of Ekman and Petterson ("Uber das Atomgewicht des Selens," *Nova Acta der K. Soc. der Wissenschäften zu Upsala*, May 13, 1876, vol x., unpaged).

The operations for the purification, as carried out by these chemists, are as follows:—

1. Solution of crude selenion in nitric acid.
2. Expulsion of excess of acid.
3. Sublimation of selenious oxide.
4. Solution of the sublimate in water and filtration (to get rid of the very insoluble mercury selenite).
5. Precipitation of selenion by reduction with hydrochloric acid and sulphur dioxide.
6. Prolonged washing of the precipitated selenion.
7. Re-conversion of the selenion into selenious oxide and repeated sublimation in a current of air (to remove possible traces of tellurium).

In addition to a repetition of the above processes, I have investigated the analytical possibilities of the separation of tellurium from selenion, the application of the spectroscope to the testing of selenion for tellurium, the separation of the elements by sublimation of selenion dioxide, and examination of the product.

The first step was to investigate the original material for tellurium, and, if possible, to find a method of detecting that element in small quantities in presence of selenion. The best of the methods I tried was Oppenheim's (Crookes, "Select Methods of Chemical Analysis," 3rd edit., p. 422). By control experiments it was found that the limits of discrimination lay somewhere between one-tenth per cent and one-fortieth per cent of tellurium in the selenion—and this only when every precaution is taken. In some trials I used over 40 grms. weight of the original selenion in order to have the advantage of concentration of tellurium. The net result, however, was only to show that there was certainly less than one-tenth per cent Te, and probably less than one-fortieth per cent. I therefore, in the first instance, tried to obtain a spectroscopic method of detecting tellurium in presence of selenion, and for that purpose experimented with the electric arc, sparking between carbon terminals kept wet with solutions of tellurous acid and tellurium salts, Bunsen flames, &c., but in the end failed to find any line of sufficient persistence to be of service. By mixing 99 parts of very pure selenion with one part of tellurium, I failed to obtain any indication of tellurium, no matter what method I employed.

Attempts were made to separate the dioxides of selenion and tellurium by taking advantage of the great difference of solubility of the oxides; the results for small proportions of tellurium showed that a sharp separation could not be effected in this way.

Attempts to take advantage of the difference in the volatility of the oxides as practised by Ekman and Petterson were more favourable, and the results obtained indicated that a sharp separation could be made by one or at most two sublimations at 360° C.

The method was tested by mixing together 10·0098 grms. of selenion, not specially purified, and 0·09985 grm. of tellurium (bought as pure). This mixture was dissolved in nitric acid, evaporated to dryness as usual, and the residue collected and placed in a platinum boat in a wide glass tube. The tube was kept at a dull red heat, and a stream of dried and filtered air was passed slowly over it. The sublimate was then re-sublimed at from 290° to 320° C. to a spot further along the tube, and it was found that the re-sublimation of the first sublimate was complete, showing that nothing had been carried forward mechanically. During this process a trace of red selenion was formed—a thing which Ekman and Petterson have shown is not to be avoided, whatever care in eliminating dust may be taken. The second sublimate was dissolved in water, and the solution filtered (though it was practically clear), boiled with hydrochloric acid, saturated with sodium bisulphite, and left to stand for fifteen hours. The precipitated elements were washed, ground, and re-washed, and finally treated by the Oppenheim method of separation. This showed that no tellurium was present within the limits mentioned. The residue in the boat containing the metallic impurities was treated for the recovery of tellurium, and 0·0975 grm. of tellurium was recovered and weighed. The loss of tellurium from all causes in this rather complicated treatment was therefore 0·00233 grm. Taking everything into consideration this loss appeared to be within the limits of the experimental error. The important fact was that the oxide of selenion sublimed at the lowest visible red heat was totally re-sublimed at a temperature below 320° without any visible residue being left behind. So far as analysis can show, therefore, it appears that sublimation of the oxides affords a method of separation of the elements—though it cannot, of course, be a theoretically perfect method, for the oxide of tellurium must have some vapour pressure at 300° C.

Preparation of Purified Selenion.

Quantities of 335 grms. of bought selenion were treated in each operation.

The material, ground to a fairly fine powder and sieved, was dissolved in nitric acid, the acid removed, and the aqueous solution of selenious acid filtered. The filtrate was evaporated to dryness, and the oxide sublimed in dry and dust-free air at 360° C. To effect the sublimation, the oxide of selenion was introduced into a 3 cm. tube in a large platinum boat, and sublimation proceeded with till the tube got blocked up. The boat was then withdrawn, and the sublimate washed out of the tube by platinum distilled water. The air was filtered through long tubes containing cotton-wool, and dried, first by calcium chloride, and then by pure strong sulphuric acid. During the sublimation a certain amount of reduction always took place at first—while traces of water were being given off and an evil-smelling gas (H_2Se?) was evolved in small quantity. On re-subliming a portion of the sublimate, there was no further reduction or evolution of gas.

The sublimed selenium dioxide was dissolved to an almost absolutely clear and colourless solution in platinum distilled water, and this was then filtered and boiled with much water containing one-ninth of its volume of strong hydrochloric acid, and the selenion precipitated at the air

* A Paper read before the Royal Society, February 14, 1907.

temperature by sulphur dioxide which had passed through several wash-bottles and finally through a solution of silver nitrate. Sulphur dioxide was at first prepared from copper and sulphuric acid, and though there was no milkiness in the wash-bottles or darkening of the precipitated silver sulphite, it was feared that some sulphuretted hydrogen might possibly be formed, and therefore recourse was had, first to the production of the gas from sodium bisulphite, and finally to its production from the combustion of very pure sulphur. In the latter case rather elaborate arrangements were required. The sulphur was burned in a large sheet-iron cylindrical vessel, provided with a zinc tray containing the sulphur. The gases coming from the chamber passed in order through a glass tube 7 feet long; a plug of glass-wool, a Liebig's condenser, Woolfe's bottle containing distilled water, a plug of cotton-wool 2 inches long, a tube containing more cotton-wool and copper turnings; a tight plug of glass-wool (to filter off the dust from the cotton-wool if any was produced), and a long tube containing copper and silver-foil. The precipitation vessel was closed, and communicated with a suction pump, whereby the gases were drawn through the system. Most of the selenion prepared was precipitated by sulphur dioxide, prepared as described.

The operation of precipitating selenion is not complete for some time. The fine red powder of selenion (which is free from lumps or coagulated portions when the precipitation has been carried out without appreciable rise of temperature) was washed on a platinum-cone, and then exhibits many of the characteristics of a gelatinous substance; for instance, it could be got to vibrate when distorted, just like a jelly.

The washing is continued till some time after no trace of hydrochloric or sulphuric acid can be detected in the washings. The fine selenion is then coagulated to some extent by starting the filtering pump, which causes it to occupy a much reduced volume, and finally dried in a dish in a water-bath, when a great deal of water separates and the selenion coagulates and becomes dark in colour. No HCl or H_2SO_3 could be found in the water which separated.

The drying is continued till the mass can be broken up, when it is again heated in a water-oven, and finally placed in a vacuum desiccator.

When the selenion appeared to be dry, it was distilled in a current of air residue in a hard glass retort protected by a fire-clay and asbestos coating.

The air residue, consisting for the most part of nitrogen, was produced as described in a previous paper (*Phil. Mag.*, Series 5, January 1, 1893, vol. xxxv., p. 1).

In spite of all precautions, some oxide of selenion appeared in the receiver, and this was as far as possible caused to deposit on the top of the receiver by keeping the selenion hot, but of course there is no certainty that it was all concentrated there.

An attempt was made to get rid of SeO_2 by re-distilling the selenion from bulb to bulb *in vacuo* in a tube blown with three bulbs. The first bulb was charged with some of the distilled selenion which had come over first, the tube was pumped out by a Sprengel pump, and filled with the air residue, and was also provided with a piece of metallic magnesium at one end. The magnesium was heated both during pumping and later, when the tube was sealed off. The tube was heated while still in connection with the pump, and as the selenion melted it just gave enough gas to change the sound of the pump, but not enough to examine—it was estimated at less than one-twentieth of the volume of the selenion (say, one-tenth cc.). There was sufficient selenion dioxide driven off by heating the selenion to form a visible deposit on the next bulb of the tube. Now the heating may be considered to have taken place under conditions precluding the presence of any appreciable amount of oxygen in the high vacuum attained in presence of hot magnesium, so we must conclude that the selenion, as prepared in bulk, either contains some oxide, or oxidises during removal and storage at ordinary temperatures. Even if it had been practicable to heat all the selenion in a high vacuum, there is no evidence that all the oxide could be separated, and no test can be made to establish with certainty that oxide is absent, even after such treatment (see below). I was therefore obliged to abandon the scheme of treating selenion as a simple elemental body for conductivity experiments.

The selenion, prepared in the manner described above, was tested in the following way—it being recognised that both arsenic and mercury, besides unknown elements, might be present.

Samples of about 10 grms. weight were dissolved in strong nitric acid, the acid evaporated with constant additions of water on the water-bath, and the dry selenion dioxide dissolved in water. In all cases the nitric acid solution was absolutely clear and left no residue. The aqueous solution was just visibly opalescent, possibly through a slight reduction of the selenious acid by dust or owing to the presence of mercury selenite.

There appears to be some question as to the reliability of the modern methods of testing for arsenic in presence of selenium (Berry, *Journ. Chem. Soc. Ind.*, 1901, p. 322). After some preliminary trials, the following method was adopted:—

Ten grms. of selenium were converted into selenious acid and dissolved in water. The solution was mixed with a large excess of a solution of ferrous chloride, and distilled in presence of a stream of hydrochloric acid gas bubbled through the apparatus. Water was added till the distillate measured three times the volume of the original mixture put into the retort. The distillates were divided into four portions, of which the first and last were much smaller than the second and third. All distillates were saturated with H_2S with all precautions, and filtered. The precipitates (visible or invisible) were dissolved in small quantities of 20 per cent solution of pure sodium hydrate, acidified with sulphuric acid, boiled with potassium meta-bisulphite, and used in the electrolytic arsenic apparatus of Dr. Thorpe (*Trans. Chem. Soc.*, 1903, vol. lxxxiii., 969).

The first distillate was from the ferrous chloride and hydrochloric acid only, and showed no arsenic, the second and third gave arsenic mirrors, and the fourth no mirror.

The total arsenic collected amounted to 0·05 mgrm. As_2O_3 or 0·00038 per cent arsenic in the material tested.

Check experiments were made to test whether the selenion, in being reduced by the ferrous chloride and hydrochloric acid, prevents arsenic from distilling over, and whether the Thorpe apparatus gives a correct result for a solution of selenide of arsenic when treated as above. The result of these tests was to show that the ferrous chloride distillation is effective in causing the arsenic to pass into the distillate, and that the arsenic is properly shown by the Thorpe apparatus. I have to thank Mr. T. H. Waller for suggesting the distillation with ferrous chloride and hydrochloric acid.

Testing for Mercury.—This is a matter of some difficulty, but the fact that an almost absolutely clear solution of selenious acid was obtained precludes the possibility of the presence of more than very minute quantities. Two methods of testing were employed.

In the first, 10 grms. of selenion were converted into sodium seleniate—or at all events selenious acid was neutralised with sodium hydrate and the product dried. The dry salt was then heated in a tube between plugs of glass-wool to a bright red heat in a current of purified and dried air just sufficient to ensure that anything capable of subliming should be carried into the cool part of the tube. The result was a large sublimate of selenious oxide. This sublimate was dissolved in water, saturated with excess of precipitated carbonate of calcium, dried on the water-bath, and re-heated in a hard glass tube, as before, first to a dull and afterwards to a bright red heat. The cold part of the tube contained a just visible sublimate. Mercury was tested for by Marcel's method (*Comptes Rendus*), using one strip of paper saturated with ammoniacal silver nitrate, and another saturated with hydrochloroplatinic acid. The paper

saturated with the silver compound did darken as the sublimate was chased up to it by a flame, but the appearance was not that produced by mercury, as shown in a check experiment; the platinum paper was not affected. This is a very sensitive test for mercury as claimed by Marcel.

The second investigation was kindly made for me by Dr. H. Sand, of Nottingham, by means of a rotating cathode which he has studied in regard to the separation of metals by electrolysis at carefully regulated voltages. About 11 grms. of the purified selenion were converted into selenious acid—acidified with nitric acid, and electrolysed under the conditions known to precipitate mercury from other salts—on to the rotating cathode. After an hour's work no deposit could be detected on the cathode, so it was made an anode in a small quantity of dilute nitric acid, and a current passed to a fine platinum-wire cathode. No mercury was deposited on the fine wire.

The sensitiveness of the method has not been communicated to me by Dr. Sand, but it probably is sensitive enough to show the presence of small quantities of mercury. We may conclude that either there is no mercury in the purified selenion, or if there is it is probably of the order of the arsenic content.

A sample of the selenion which had been used by Messrs. Mason and Vonwiller was returned to me for examination towards the end of 1906, and was examined by solution in nitric acid, &c. Nothing large enough to weigh could be extracted from 10 grm. samples, but there was, nevertheless, evidence that the selenion had picked up some impurities in the varied experiments which had been made upon it. Originally it was some of the purified and distilled product described above. There was a trace of organic matter separable from the nitric acid solution, and a few specks of insoluble white matter in the aqueous solution of selenious acid. There was also a trace of iron and alumina. The result of treating the filtrate from selenion precipitated by hydrochloric acid and sulphur dioxide with sulphuretted hydrogen was a minute dark coloured precipitate which was tested in the usual way, but could not, owing to its small quantity, be satisfactorily examined. Special tests for gold and platinum showed that it was not the latter, the former doubtful, and it did not appear to be mercury. Taking all the residues and precipitates together, the total weight could not have been more than 1 or 2 mgrms. My opinion is that the contamination consisted mainly of dust with a trace of mercury or gold, and some hydrocarbon—possibly oil or paraffin.

In letters of October 30 and November 19, Professor Pollock informs me that the selenion was, in fact, floated on mercury in some of the experiments and gilded in others, and the material had been re-melted at least a dozen times, so some contamination was to be expected. I made a special investigation for zinc, as Messrs. Mason and Vonwiller state that the selenion was melted in a zinc vessel, but the material was found absolutely free from this element, at all events to tests by potassium ferrocyanide and sodium sulphide, which are fairly delicate.

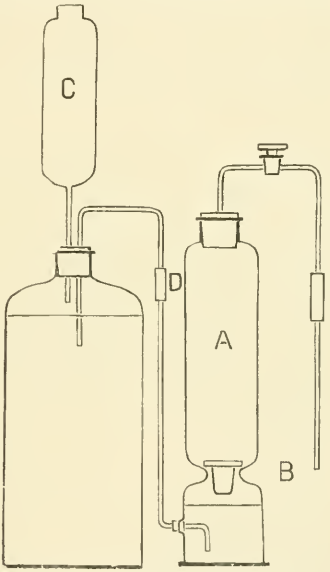
A test for SeO_2 was made in the following manner:—About 4 grms. of the selenion was placed in a hard glass tube 1 cm. diameter, drawn out to a long point—about 20 cm. long and 2 mm. diameter. The tube was connected with an apparatus for supplying hydrogen absolutely freed from oxygen, and was filled and pumped out many times. Finally, the pressure was reduced to about 30 mm. mercury, and sufficient hydrogen allowed to enter to insure that sublimates would be carried into the narrow part of the tube. A just visible sublimate of SeO_2 was observed. On repeating the trial with the same selenion to which 1 mgrm. of SeO_2 had been added; the sublimate was, at least, doubled, and, on adding 4 mgrms., a comparatively large sublimate was obtained, but it was almost instantly covered over by a deposit of selenion, or was reduced and thus removed. I think it is safe to conclude that 4 grms. of the selenion used by Vonwiller and Mason did not contain anything like 5 mgrms. of SeO_2, and probably only about 1 mgrm., but the test is not entirely satisfactory.

My thanks are due to Dr. George Elliot, of Sydney, for his kindness in supplying me with considerable quantities of specially purified acids.

AN IMPROVED GAS GENERATOR.

By F. SOUTHERDEN, B.Sc., F.I.C.

The general construction of this apparatus is apparent from the figure. A is a "lime tower," about 12 inches in height, the upper portion of which is packed with the solid reagent, a flat stopper with the top partially chipped away, fitting quite loosely at B. The liquid reagent is contained in a "Winchester quart" bottle connected to A by a syphon tube; and since this tube does not reach far below the surface, fresh liquid always syphons into A, the denser spent liquor sinking, as returned, towards the bottom of the reservoir. The stem of the funnel, C, reaches to such a point that, as the liquid sinks in the lower bulb of A, the corresponding rise of level in the reservoir causes liquid to enter the funnel, so that if through vigorous action the syphon empties, it automatically re-fills when next required.



Should the tap be left turned on, only the liquid in A becomes exhausted, and to re-start it is merely necessary first to slope the whole apparatus, so that most of the liquid syphons back from A into the reservoir. A rubber tube at D renders the connection between the vessels more flexible, and by arranging it above the level in the bottle all possibility of mess, consequent on leakage, is avoided.

The apparatus has proved specially useful where a moderate supply of gas is very frequently required, *e.g.*, as a generator of sulphuretted hydrogen. Though less portable than the ordinary Kipp's apparatus, it requires much less attention on account of the very large acid reservoir, and the replenishing of acid or sulphide is more conveniently and rapidly carried out.

Royal Albert Memorial College, Exeter.

FOURTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS.

DETERMINATIONS PUBLISHED DURING 1906.*

By F. W. CLARKE.

DURING 1906 there was a remarkable activity among the workers upon atomic weights, and many new determinations were published. Brief summaries of the new data are given in the following pages.

Nitrogen.

Three papers on the atomic weight of nitrogen have appeared during 1906, but they are essentially critical and contain no new determinations. First, Guye has summed up all the recent work upon this constant, and shown that it cannot vary much from 14·01 (*Ber.*, xxxix., 1470). Gray (*Journ. Chem. Soc.*, lxxxix., 1173) has subjected Stas' determinations to a searching criticism, and attempted to discover their possible source of error. Various alternatives are suggested, but no definite conclusion is reached. Scott (*Proc. Chem. Soc.*, xxi., 300) has re-discussed his old analyses of ammonium chloride and bromide (*Journ. Chem. Soc.*, lxxix., 147), which were discordant, and finds that upon applying the new value for chlorine to them (Cl = 35·473) the disagreement vanishes. On this basis his figures give, from NH_4Br, N = 14·010, and from NH_4Cl, N = 14·013. These figures are in harmony with the modern physico-chemical determinations.

Silver.

The accepted value for the atomic weight of silver rests upon analyses of chlorates, bromates, and iodates, and upon the ratios between the figures thus obtained for the halides and the ratios of the latter to silver. The chief pair of ratios is that of $KClO_3$: KCl and KCl : Ag, from which, when O = 16, Ag = 107·927.

The potassium chlorate ratio has now been re-investigated by Guye and Ter Gazarian (*Comptes Rendus*, cxliii., 411), who find that the crystallised salt contains a constant impurity of KCl, amounting to 2·7 parts in 10,000. This contamination was overlooked by Stas, and when it is taken into account the atomic weight of silver is reduced to 107·879.

With this datum, the modern atomic weights for nitrogen and carbon, and Dixon and Edgar's value for chlorine, the authors have re-computed the atomic weight of silver from data already existing. The results of the re-calculation are as follows:—

Ag : $AgNO_3$	Ag = 107·882
Ag : $AgC_2H_3O_2$	107·886
Ag : $AgC_7H_6O_2$	107·888
Ag : NH_4Cl	107·871
Ag : Cl	107·895
N_2O_5 : Cs_2O and Ag : CsCl	107·885
N_2O_5 : K_2O and Ag : KCl	107·901
$KClO_3$: KCl and Ag : KCl	107·879
$AgClO_3$: AgCl and Cl : H	107·908
$AgClO_3$: AgCl and Ag : AgCl ..	107·905
Mean	107·890

The concordance of these values is most striking, and the argument for a lower atomic weight for silver is very strong.

In another paper, discussing some of the same evidence, Guye (*Journ. Chim. Phys.*, iv., 174) has pointed out the necessity for a general revision of the atomic weights upon the basis of modern physico-chemical data. He also calls attention to the remarkable experiments of Landolt and others on apparent changes of weight during chemical reactions, and shows that in any general discussion of atomic weights, investigations of that order should be taken into account.

Chlorine.

Guye and Ter Gazarian (*Comptes Rendus*, cxliii., 1233) have determined the density of HCl. At 0°, 760 mm., sea level, and lat. 45°, one litre of the gas weighs, in grms.—

1·6404
1·6397
1·6389
1·6401
Mean .. .. 1·6398

Reducing this value by means of the critical constants, the authors find Cl = 35·461. This agrees closely with the gravimetric determination of Dixon and Edgar.

Bromine.

The atomic weight of bromine, referred to Ag = 107·93 and Cl = 35·473, has been carefully re-determined by Baxter (*Journ. Am. Chem. Soc.*, xxviii., 1322). First, the ratio Ag : AgBr was measured. The data are given below, with weights reduced to a vacuum.

Weight Ag.	Weight AgBr.	Atomic weight Br.
4·71853	8·21363	79·946
5·01725	8·73393	79·952
5·96818	10·38932	79·953
5·62992	9·80039	79·951
8·13612	14·16334	79·954
5·07238	8·82997	79·954
4·80711	8·36827	79·956
4·27279	7·43776	79·947
5·86115	10·20299	79·953
7·91425	13·77736	79·958
6·40765	11·15468	79·959
6·38180	11·10930	79·952
6·23696	10·85722	79·953
9·18778	15·99392	79·953
8·01216	13·94826	79·953
10·48638	18·25452	79·953
8·59260	14·95797	79·954
8·97307	15·62022	79·953
	Mean	79·953

Secondly, silver bromide was transformed into chloride by heating in a current of chlorine. The corrected data are as follows:—

Weight AgBr.	Weight AgCl.	Atomic weight Br.
8·03979	6·13642	79·953
8·57738	6·54677	79·952
13·15698	10·04221	79·952
12·71403	9·70413	79·952
13·96784	10·66116	79·951
13·08168	9·98469	79·953
12·52604	9·56059	79·953
11·11984	8·48733	79·952
8·82272	6·73402	79·953
11·93192	9·10721	79·951
12·53547	9·56767	79·955
17·15021	13·09009	79·952
10·31852	7·87572	79·952
	Mean	79·952

The value Br = 79·953 is the one finally adopted.

Iodine.

The electro-chemical equivalent of iodine has been measured by Gallo (*Gazz. Chim. Ital.*, xxxvi., 116). Iodine was liberated electrolytically from a solution of potassium iodide, and determined by titration with sodium thiosulphate. In the same circuit silver was deposited in a silver voltameter. The equivalent weights, reduced to a

* From the *Journal of the American Chemical Society*, xxix., No. 3.

vacuum, and with values for I referred to Ag = 107·93, are given below.

Weight Ag.	Weight I.	Atomic weight I.
0·18054	0·21230	126·92
0·21360	0·251309	126·98
0·23103	0·27181	126·90
0·24005	0·28213	126·85
0·15454	0·18167	126·85
0·2597	0·30515	126·82
0·16229	0·19080	126·89
0·300988	0·35411	126·98
0·26819	0·31528	126·88
0·25877	0·30425	126·90
0·24422	0·28703	126·85
0·20838	0·24516	126·92
0·25047	0·29445	126·88
0·20266	0·23826	126·89
0·18316	0·21533	126·89
0·27278	0·43809	126·84
0·28221	0·33207	126·90
0·2582	0·30356	126·89
0·33963	0·39923	126·88
0·33461	0·39345	126·91
0·3360	0·39502	126·89
0·37025	0·43526	126·88
0·30824	0·36233	126·87
0·36390	0·42789	126·91
	Mean	126·89

The values found are not very concordant, and the determination can hardly be given much weight when compared with the recent measurements by Baxter.

Potassium.

The ratios connecting potassium chloride with silver and silver chloride have been re-determined by Richards and Staehler (*Ber.*, xxxix., 3611). The data are as follows, with vacuum weights :—

First, Ag : KCl :: 1 : *x*.

Weight KCl.	Weight Ag.	Ratio.
2·35178	3·40295	0·681100
1·97348	2·85582	0·691038
3·88074	5·61536	0·691094
7·44388	10·77156	0·691068
5·00681	7·24514	0·691058
5·04833	7·30515	0·691065
8·19225	11·85412	0·691089
4·99795	7·23230	0·691060
5·16262	7·47042	0·691075
	Mean	0·691072

Hence, if Ag = 107·93 and Cl = 35·473, K = 39·114.

The first two experiments are regarded as preliminary.

Second, AgCl : KCl :: 1 : *x*.

Weight KCl.	Weight AgCl.	Ratio.
(*a*) 3·88672	7·47271	0·520122
(*a*) 3·47292	6·67680	0·520147
(*a*) 8·75449	16·83071	0·520150
4·36825	8·39858	0·520118
5·56737	10·70384	0·520128
6·41424	12·33228	0·520120
3·27215	6·29126	0·520110
4·83028	9·28702	0·520111
	Mean of last five	0·520118

(*a*) Preliminary determinations, not included in the mean.

Hence, K = 39·114.

Sodium.

Incidentally to a paper upon the transition temperature of sodium bromide, Richards and Wells (*Proc. Amer. Acad.*, xli., 443) give two determinations of the ratio AgBr : NaBr :: 1 : *x*. The data with vacuum weights are—

Weight NaBr.	Weight AgBr.	Ratio.
5·49797	10·03253	0·54814
3·64559	6·65248	0·54805

If Ag = 107·93 and Br = 79·955, Na = 23·008—a value in agreement with that previously found from analyses of sodium chloride.

Manganese.

Baxter and Hines (*Journ. Am. Chem. Soc.*, xxviii., 1560) have revised the atomic weight of manganese through analyses of the chloride and bromide. The data with reference to the chloride are as follows :—

Weight $MnCl_2$.	Weight AgCl.	Weight Ag.	Atomic weight Mn. AgCl ratio.	Atomic weight Mn. Ag ratio.
4·62970	10·54641	7·93740	54·957	54·960
3·52899	8·03868	6·05041	54·962	54·958
3·30881	7·53731	5·67279	54·959	54·960
3·56843	8·12932	6·11818	54·950	54·955
3·45083	7·86129	5·91637	54·952	54·958
4·47948	10·20372	7·67995	54·963	54·959
3·92089	8·93140	6·72227	54·962	54·958
	Mean		54·958	54·958

All weights are reduced to a vacuum, and computations were based upon Ag = 107·93 and Cl = 35·473. The bromide series gave the following results when Br = 79·953 :—

Weight $MnBr_2$.	Weight AgBr.	Weight Ag.	Atomic weight Mo. AgBr ratio.	Atomic weight Mo. Ag ratio.
5·58416	9·76561	—	54·964	—
5·63432	9·85345	—	54·961	—
6·53738	11·43300	6·56755	54·957	54·962
4·81005	8·41206	4·83238	54·959	54·957
4·88097	8·53642	4·90354	54·950	54·960
5·63219	9·85008	5·65813	54·954	54·964
6·52626	11·41293	—	54·968	—
5·79924	10·14206	5·82600	54·957	54·963
3·59809	6·29271	3·61478	54·952	54·957
5·16334	9·02959	5·18711	54·966	54·965
3·92226	6·85968	3·94042	54·951	54·959
4·49158	7·85571	4·51250	54·942	54·953
3·60071	6·29740	3·61736	54·949	54·960
4·77392	8·34915	4·79620	54·951	54·951
3·57660	6·25569	3·59319	*54·933	54·957
5·69972	9·96840	5·72641	54·947	54·948
6·58983	—	6·62041	—	54·957
4·19911	—	4·21839	—	54·967
Mean, rejecting the starred value ..			54·955	54·959
Mean of both series				54·957

Cobalt.

The determinations by Baxter and Coffin of the atomic weight of cobalt are based upon analyses of the chloride (*Journ. Am. Chem. Soc.*, xxviii., 1560). The data are subjoined, with corrected weights, and reduced with Ag = 107·93 and Cl = 35·473.

Weight $CoCl_2$.	Weight AgCl.	Weight Ag.	Atomic weight Co. AgCl ratio	Atomic weight Co. Ag ratio.
1·09959	2·42676	1·82671	59·009	58·991
1·47733	3·26095	2·45398	58·988	59·005
3·84133	8·47735	6·38081	59·014	59·005
2·96315	6·54019	4·92244	58·997	58·995
3·48418	7·69084	5·78815	58·986	58·991
3·29523	7·27284	5·47410	59·002	58·995
1·57655	3·48012	2·61905	58·982	58·992
3·64342	—	6·05232	—	58·999
	Mean		58·997	58·997

Hence Co varies from the round number 59 only within the limits of experimental uncertainty.

(To be continued).

DECOMPOSITION OF CHLORAL HYDRATE BY CAUSTIC SODA.

By FRANK E. WESTON, B.Sc., and HENRY R. ELLIS, B.Sc.

Having observed discrepancies in the estimation of chloral hydrate by caustic soda, the following investigation was carried out to determine when the equation $CCl_3CH(OH)_2 + NaOH = CHCl_3 + HCOONa$ is true.

In certain text-books (Perkin and Kipping) this equation is given to represent the action of boiling alkalis on chloral hydrate; this statement is erroneous, the reaction under these conditions consisting of two distinct reactions:—

$$CCl_3CH(OH)_2 + NaOH = CHCl_3 + HCOONa + H_2O \quad . \; . \; 1.$$

$$CHCl_3 + 4NaOH = 3NaCl + HCOONa + 4H_2O \; . \; . \; 2.$$

The second reaction is not complete, owing to the volatility of the $CHCl_3$; if this body is not allowed to escape, the equation representing the total change may be given as $CCl_3CH(OH)_2 + 5NaOH = 2HCOONa + 5H_2O + 3NaCl$.

The chloroform is decomposed at temperatures from 40° C. upwards, and this causes low results when the liberated $CHCl_3$ is estimated by passing it over red-hot lime in the usual manner ("Mann's Forensic Medicine and Toxicology"). If the chloral hydrate is estimated by NaOH, the results are too high unless low temperatures are used.

When the chloral was decomposed by Na_2CO_3 the decomposition of the liberated $CHCl_3$ was much less.

The NaOH used was obtained from metallic sodium (the Na was exposed to a moist atmosphere free from CO_2) and was quite free from chlorides.

The chloral hydrate used was supplied by Kahlbaum, and the solution used contained 30 grms. per litre.

Constant Temperature (18° C.), *Times varying.*

	Time.	Chloral hydrate.	N. NaOH.	N. H_2SO_4.	Mean.	NaOH used.
	Minutes.	Cc.	Cc.	Cc.	Cc.	Cc.
1.	2	20	25	21·4	21·4	3·6
	2	20	25	21·4		
	(*a*) 2	20	25	21·4		
2.	5	20	25	21·3	21·29	3·71
	5	20	25	21·3		
	(*a*) 5	20	25	21·275		
3.	10	20	25	21·075	21·1	3·9
	10	20	25	21·075		
	(*a*) 10	20	25	21·15		
4.	20	20	25	21·125	22·075	3·925
	20	20	25	21·075		
	(*a*) 20	20	25	21·025		
5.	40	20	25	21	21·00	4·0
	40	20	25	21		
	(*a*) 40	20	25	21·025		
6.	80	20	25	20·975	20·94	4·06
	80	20	25	20·925		
	(*a*) 80	20	25	20·925		
7.	200	20	25	20·55	20·44	4·56
	200	20	25	20·44		
	(*a*) 200	20	25	20·325		
8.	2000	20	25	19·35	19·3	5·7
	2000	20	25	19·25		
	(*a*) 2000	20	25	19·3		
9.	7200	20	25	16·525	16·54	8·46
	7200	20	25	16·525		
	(*a*) 7200	20	25	16·675		

(*a*) The $CHCl_3$ not shaken out of the solution.

Conclusions.

1. The caustic soda present very slowly attacks the chloroform, which is liberated from the chloral hydrate with the formation of sodium formate and sodium chloride.

2. It is unnecessary to shake the solution until the turbidity disappears.

3. If the reaction takes place in the cold, it proceeds in accordance with the usual equation:—

$$CCl_3CH(OH)_2 + NaOH = CHCl_3 + H.COONa + H_2O.$$

The decomposition of the $CHCl_3$ then proceeds so slowly that it exerts little influence on the result until some time has elapsed.

Experiments at Varying Temperatures.

The NaOH solution was heated to the desired temperature on a water-bath and the chloral hydrate solution run in quickly; as soon as the turbidity disappeared the remaining caustic soda estimated (after cooling quickly) by N. H_2SO_4, and the chloride by N/10 $AgNO_3$.

	Temp.	Chloral hydrate.	N. NaOH.	Means of several titrations. N. H_2SO_4.	Means of several titrations. N. NaOH used.	N/10 $AgNO_3$.
	°C.	Cc.	Cc.	Cc.	Cc.	Cc.
1.	0	20	25	21·6	3·5	—
2.	15	20	25	21·4	3·6	—
3.	20	20	25	21·4	3·6	—
				21·4	3·6	—
4.	40	20	25	20·625	4·375	—
				20·6	4·4	—
5.	50	20	25	20·6	4·4	2·94
				20·6	4·4	2·96
6.	70	20	25	18·2	6·8	20·7
				18·2	6·8	20·7
7.	80	20	25	17·3	7·7	32·25
8.	90	20	25	14·5	10·5	59·825
9.	100	20	25	13·425	11·575	66·5
				14·525	10·5	57·95
				11·75	13·25	79·575

Results.

The NaOH attacks the $CHCl_3$ liberated, the amount of $CHCl_3$ transformed below 50° C. being small.

The $CHCl_3$ seems to be decomposed in accordance with the equation $CHCl_3 + 4NaOH = HCOONa + 3H_2O + 3NaCl$. A formate was found in the residue after boiling $CHCl_3$ with NaOH for a short time.

Caustic Soda run into Warm Solution of Chloral Hydrate Solution at Varying Temperatures.

The flask was shaken until turbidity disappeared, cooled, and the excess of alkali determined by N. H_2SO_4, and the sodium chloride by N/10 $AgNO_3$.

	Temp.	Chloral hydrate.	N. NaOH.	Mean of several titrations. N. H_2SO_4.	Mean of several titrations. N. NaOH used.	N/10 $AgNO_3$.
	°C.	Cc.	Cc.	Cc.	Cc.	Cc.
1.	40	20	25	20·025	—	—
				20·05	—	—
2.	50	20	25	20·55	4·45	2·425
				20·6	4·4	2·525
3.	70	20	25	19·725	5·275	13·675
4.	80	20	25	18·925	6·075	18·45
5.	90	20	25	16·15	8·85	45·05
6.	100	20	35	18·85	6·15	23·6

Conclusions.

The chloral is volatile in steam, hence these readings are all much less than the others obtained when chloral was run into warm caustic soda solutions.

Reaction between Boiling NaOH *and Chloral Hydrate.*

	Chloral (cc.).	N. NaOH (cc.).	N. H_2SO_4 (cc.).	NaOH used (cc.).	N/10 $AgNO_3$ (cc.)
Experiment 1.—Chloral hydrate dropped from burette to boiling NaOH in open flask, cooled as soon as the amount required had been added, and at once titrated against H_2SO_4	20	25	14·65	10·15 (6·65)	52
Experiment 2.—Same as No. 1, chloral hydrate added more slowly	20	25	12·1	12·9 (9·1)	78·2
Experiment 3.—The two solutions mixed cold and boiled together for one hour	20	25	11·45	13·55 (10·05)	78·8
	20	25	10·6	14·4 (11·9)	86·2
Experiment 4.—The chloral hydrate solution dropped slowly through a reflux condenser to the boiling caustic soda and boiled for one hour	20	25	14·2	10·8 (7·3)	59·6
	20	25	13·1	11·9 (8·4)	58·35
Experiment 5.—The chloral hydrate added slowly to the bottom of the boiling alkali solution and boiled ander a reflux condenser for a short time	20	25	11·45	13·55 (10·05)	79·275
	20	25	10·95	14·55 (11·05)	86·475

Results.

The decomposition took place more rapidly in the last experiments; since the $CHCl_3$ was liberated under the NaOH it had less chance of escaping.

By subtracting 3·5 cc. from the readings in the fourth column the number obtained is the volume of NaOH used to decompose the liberated chloroform. (These numbers are inserted in parentheses under the numbers in column 4).

The ratio between the number of cc. of N. NaOH and N. $AgNO_3$ required for each 20 cc. of chloral approximates in each case to 4 : 3, clearly showing that the $CHCl_3$ decomposes in accordance with the equation $CHCl_3 + 4NaOH = 3NaCl + HCOONa + 3H_2O$.

Similar experiments with $CHCl_3$ alone gave results in agreement with this equation.

The presence of the formate did not affect the estimation of the chloride. A solution of N 10 NaCl, containing about 8 grms. of sodium formate per litre, was estimated by means of the N 10 $AgNO_3$; in no case was any error caused by the formate.

The Chemical Laboratory,
The Polytechnic, Regent Street.

Preparation of Argon from the Air by means of Calcium Carbide.—Franz Fischer.—In order to prepare pure argon the author used a mixture of calcium carbide containing 10 per cent of calcium chloride. This absorbs nitrogen very readily at 800°, while pure carbide scarcely reacts at all at that temperature. The oxygen of the air is also absorbed by the mixture, calcium oxide and carbon being formed, and thus argon is left. The mixture is heated to 800° in strong-walled iron tubes in an ordinary gas furnace *in vacuo*. Gases are first evolved, among them acetylene, formed by the action of small quantities of water vapour given up by the calcium chloride, upon the carbide. Tarry products also distil over. When the evolution of gases ceases, dry pure air is allowed to pass in, and everything is then absorbed except argon and the other inert gases. The other products of the reaction are carbon, calcium oxide, and cyanamide.—*Berichte*, vol. xl., No. 5.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part II.—Analysis of the Silver, Copper, and Tin Groups.

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 201).

Procedures and Notes (*continued*).

Precipitation and Separation of the Copper and Tin Groups.

Procedure 21.—Treat separately as follows the various acid solutions previously obtained (P. 11, 4, 2, 5, 6, 7, 8), each of which should contain 4 cc. HCl (1·12) or 1·5 cc. H_2SO_4 (1·84), and have a volume of about 40 cc. Heat the solution in a conical flask nearly to boiling, and pass into it H_2S gas until it is saturated, and then for ten to fifteen minutes longer, keeping the solution at 70—90°. [*If the rarer elements are likely to be present, continue the precipitation in a pressure bottle as described in N. 3]. Cool the mixture; without filtering add to it 60 cc. water, completely saturate it in the cold with H_2S gas, cork the flask, shake it, and allow it to stand fifteen minutes. Filter, and wash the precipitate with hot water. (Precipitate, P. 22; filtrate, P. 61).

Notes.

1. No sharp line can be drawn between the solubilities of the sulphides of the copper and tin groups and those of the iron group; they form rather a graded series in which the solubility of each member differs from that of the next only by a greater or less amount. Since now, owing to the effect of the added acid in reducing the ionisation of the hydrogen sulphide, the solubility of any sulphide increases as the concentration of acid (or, more strictly, of hydrogen ion) in the solution increases, the line between precipitation and non-precipitation will fall at a point in the series dependent on the acid concentration and temperature. Thus, if arranged in the order in which they are precipitated from cold HCl solutions of decreasing concentration, the series is approximately as follows:—Arsenic, mercury and copper, antimony, bismuth and stannic tin, cadmium, lead and stannous tin, zinc, iron, nickel and cobalt, manganese. For reasons connected with the analysis of the separate groups, and for the reason that the separation is then a fairly sharp one, it has been found best to adjust the acid concentration so as to cause lead and stannous tin to precipitate and zinc to remain in solution.

2. The effect of acid on the precipitation of the various sulphides is explained by the Mass Action Law and Ionic Theory as follows:—When a dilute solution, whether aqueous or acid, is saturated at a definite temperature with H_2S gas under the atmospheric (or any definite pressure) the H_2S as such always has the same concentration. This ionises, however, to a slight extent into H^+ and HS^-, and to a still less extent into $2H^+$ and $S^=$. It is only the latter form of ionisation that needs to be considered here. Now between the H_2S and its ions must be maintained the equilibrium expressed by the equation $(C_{H^+})^2 \times C_{S^=} = \text{const.} \times C_{H_2S}$; or, since in this case C_{H_2S} = const., as just stated, it follows that also $(C_{H^+})^2 \times C_{S^=} = \text{const.}$ From this it is evident that when C_{H^+} is increased by the addition of acid to the solution, $C_{S^=}$ must be decreased in the proportion in which the square of C_{H^+} is increased; thus, if C_{H^+} is doubled, $C_{S^=}$ will be reduced to one-fourth. But in order that a sulphide —for example, of the formula $M^{++}S^=$— may precipitate, the concentration product $C_{M^{++}} \times C_{S^=}$ must attain a value equal to the solubility product, which is the value of this concentration product which prevails in pure water in contact with the solid sulphide. The solubility product varies, however, with the nature of the

* From the *Technology Quarterly*, xix., No. 3 September, 1906.

sulphide and with the temperature; and therefore the acid concentration that will barely permit of precipitation when C_{M++} has a definite value (for example, 1 mgrm. in 100 cc.) will be different for different sulphides and for the same sulphide at different temperatures. This acid concentration also varies with the nature of the acid, since the various acids are ionised to a different extent; thus, zinc is precipitated from a fairly concentrated solution of acetic acid, since, owing to the slight ionisation of this acid, the H^+ concentration is less than in a far more dilute solution of hydrochloric acid.

3. The solution is first saturated with H_2S at nearly the boiling temperature, because certain elements, especially arsenic in the higher state of oxidation (and the rarer elements, platinum and molybdenum), are only slowly and incompletely precipitated in the cold, and because the precipitates of almost all sulphides separate from hot solutions in a form better suited for filtration. In case precipitation seems to continue after the solution has become fully saturated with H_2S, it indicates that one of the elements just named may be present; and, to insure complete precipitation of the arsenic, the heating and passage of the gas must sometimes be continued for an hour longer. [*In the case of molybdenum and the platinum elements, it is necessary, after most of the sulphide has separated, to cool the solution, to saturate it in the cold with H_2S in a stout bottle, to stopper the bottle with a cork securely held in place by wire, and to heat the bottle in a vessel of boiling water for an hour]. The solution is at first diluted to only about 40 cc., because arsenic is more rapidly thrown out from rather strongly acid solutions, and because titanium would be precipitated as hydroxide if the solution were further diluted and were kept near the boiling temperature; moreover, bismuth and a moderate quantity of antimony do not precipitate as oxychloride at this dilution, but might do so if the solution were at once further diluted. The solution is finally diluted to 100 cc., completely saturated in the cold, and allowed to stand, in order to cause the precipitation of even 1 mgrm. of cadmium, lead, or stannous tin. Zinc, iron, nickel, and cobalt, on the other hand, do not precipitate at all under these conditions, even when 500 mgrms. are present alone; and even 1 or 2 mgrms. of any of them can be detected in the filtrate when large quantities of elements of the copper and tin groups are also present.

4. If at first a white or yellowish precipitate forms which immediately turns black with more H_2S it indicates mercury. The white compound is $HgCl_2.2HgS$, and this is converted into HgS by the excess of H_2S. An orange precipitate separating from the hot, more concentrated solution shows antimony, or much cadmium (or selenium); a yellow one, arsenic or stannic tin. A yellow precipitate separating from the cold more dilute solution shows cadmium. All the other sulphides are black or brownish black. For the composition of the H_2S precipitates, see Table V. The quantity of sulphur combined with the metallic element, however, varies with the conditions of precipitation, owing to partial reduction, in the cases of arsen*ic* arsenic and antimonic antimony [*and of gold, selenium, tellurium, and probably molybdenum]. The extent to which the sulphides are combined with water and with hydrogen sulphide is also variable, and, in general, unknown.

5. A white, finely divided precipitate of free sulphur will be formed if the solution contains substances capable of oxidising H_2S. The most important of these likely to be present are ferric salts, chromates, [*vanadates], permanganates, and chlorates. Nitric acid, if moderately concentrated, would also destroy the H_2S; and for this reason it must have been removed as directed in P. 4. The reduction by H_2S of ferric salts to ferrous is attended by a change in colour from yellow to colourless; of chromates to chromic salts, from orange to green; [*of vanadates to vanadyl salts, from yellow to blue]; and of permanganates to manganous salts, from purple to colourless.

Procedure 22.—Transfer the H_2S precipitate (P. 21) to a small casserole, add to it 10 to 25 cc. ammonium monosulphide (if the original substance was treated with HNO_3 in P. 3), or 5 to 10 cc. ammonium polysulphide (if it was dissolved in water alone), cover the dish, and warm the mixture slightly (to 40—60°) for about ten minutes with frequent stirring. Add 10 cc. water, filter, and wash once with hot water. [If the residue is considerable in amount and much has been extracted from it by this treatment, as indicated by its appearance, or as determined in P. 41, warm it again with ammonium monosulphide or polysulphide, and filter, collecting the filtrate separate from the first one]. Wash the residue thoroughly with hot water, to which, in case the precipitate tends to pass through the filter, about 5 per cent solid NH_4NO_3 should be added. (Residue, P. 23; solutions, P. 41).

Notes.

1. In separating the copper and tin groups it is better to use (colourless) ammonium monosulphide rather than (yellow) polysulphide whenever the H_2S precipitate must contain any tin and most of any antimony present in the state of the higher sulphide (SnS_2 or Sb_2S_5). This is the case when hot concentrated nitric acid was used originally in dissolving the substance, but may not be so when water alone (or HCl) was used; hence the directions as to the choice between the two solvents. The polysulphide has the disadvantage that it dissolves a not inconsiderable quantity of CuS and HgS, thus making the tests for copper and mercury less delicate, and making it more difficult to determine from the colour of the HCl precipitate obtained from the ammonium sulphide solution in P. 41 whether or not elements of the tin group are present. The polysulphide must, nevertheless, be used if tin may be present as SnS, or much antimony as Sb_2S_3; for in the monosulphide SnS is almost insoluble and Sb_2S_3 is only moderately soluble (50 to 100 mgrms. Sb in 10 cc. of the reagent).

2. In order that the separation of the copper and tin groups by ammonium sulphide may be as complete as possible, it is necessary to employ a concentrated reagent highly charged with hydrogen sulphide, and containing, in the case of the polysulphide, an appropriate excess of sulphur. Suitable reagents are prepared by completely saturating a measured volume of NH_4OH of specific gravity 0·90 with H_2S in the cold, adding a fresh portion of NH_4OH (0·90) equal to two-thirds of the original volume, and diluting the mixture with an equal volume of water. From this solution, which constitutes "ammonium monosulphide," the "ammonium polysulphide" is prepared by dissolving in 1 litre of it 25 grms. of flowers of sulphur. These reagents, especially the monosulphide, should be kept as far as possible out of contact with the air, which is conveniently done by storing them in small, completely filled, glass-stoppered bottles, for the oxygen of the air destroys the sulphide with liberation of sulphur, which at first combines with the still unchanged sulphide, but precipitates later when the oxidation becomes more complete. The monosulphide reagent is a solution of $(NH_4)_2S$, and of the products of its hydrolysis, NH_4SH, NH_4OH, and a little H_2S. The polysulphide contains in addition various polysulphides of the forms $(NH_4)_2S_{2-5}$ and $(NH_4)HS_{2-5}$ in unknown proportions.

3. The action of ammonium sulphide in dissolving the sulphides of the tin group depends on the formation of soluble salts of sulphoacids with complex anions. When the monosulphide is used the reactions are as follows:—

$$\left.\begin{matrix}As_2S_3\\Sb_2S_3\end{matrix}\right\} + 3(NH_4)_2S = 2\left\{\begin{matrix}(NH_4^+)_3AsS_3^{\equiv}\\(NH_4^+)_3SbS_3^{\equiv}\end{matrix}\right\}$$

$$\left.\begin{matrix}As_2S_5\\Sb_2S_5\end{matrix}\right\} + 3(NH_4)_2S = 2\left\{\begin{matrix}(NH_4^+)_3AsS_4^{\equiv}\\(NH_4^+)_3SbS_4^{\equiv}\end{matrix}\right\}$$

$$SnS_2 + (NH_4)_2S = (NH_4^+)_2SnS_3^{=}$$

The excess of sulphur in the polysulphide oxidises the lower sulphides (As_2S_3, Sb_2S_3, SnS) to the same sulpho-salts as are obtained by dissolving the higher sulphides (As_2S_5, Sb_2S_5, SnS_2) in ammonium monosulphide. It will be seen that these sulpho-salts are analogous to the salts of the familiar oxygen acids of these elements, the difference being that sulphur has replaced oxygen. Analogous sulpho-salts are formed with platinum, gold, and molybdenum, such as $(NH_4)_2PtS_3$, $(NH_4)_3AuS_3$, and $(NH_4)_2MoS_4$. Tellurium and selenium probably form similar compounds; but they may also combine directly with the ammonium sulphide in the same way as sulphur does, forming such compounds as $(NH_4)_2SSe_x$.

4. When ammonium monosulphide is used 500 mgrms. of any of the comman tin-group elements, in the form of higher sulphide, dissolve in 25 cc. of the reagent, provided this has been described in N. 2. When the polysulphide is used, 500 mgrms. of any of the common tin-group elements, whether present as the higher or lower sulphide, dissolve in 10 cc. of the reagent. The quantity of SnS and Sb_2S_3 dissolved by the polysulphide increases with its concentration and the excess of sulphur which it contains. A reagent containing a greater excess of sulphur is not used, however, since this would dissolve more CuS and HgS.

5. Of the rarer elements, gold and platinum divide themselves in the ammonium sulphide treatment between the solution and the residue in a proportion which depends in large measure on the other elements which are present with them. They may therefore be found mainly either with the copper or with the tin group, and should be tested for in the course of the analysis of each group. Molybdenum dissolves in moderate quantity in either ammonium monosulphide or polysulphide, but when a quantity as large as 50 mgrms. is present much of it remains with the copper group; yet there is no danger of not finding a considerable part of it in the tin-group solution, and its presence in the copper-group residue does not interfere with the detection of any of the elements, since it is not precipitated by any of the reagents used. When molybdenum is present, even in as small a quantity as 1 mgrm., the ammonium sulphide solution has an orange-red colour; and this becomes very deep when a moderate quantity is present. Selenium and tellurium pass completely, or almost completely, into the ammonium sulphide solution.

6. Even when a quantity of only 1 or 2 mgrms. of arsenic or antimony is present with a large quantity (even 500 mgrms.) of an element of the copper group, enough is extracted by either the monosulphide or polysulphide to be detected in the subsequent tests. With tin, however, the separation is imperfect; for, when a large quantity of elements of the copper group and only 3 to 5 mgrms. of tin are present, the whole of this may remain undissolved; indeed, when much cadmium is present and the tin is in the stannous state, as much as 15 mgrms. of the latter may be wholly left in the residue, even when the polysulphide is used. On this account it is necessary to test for tin in the course of the analysis of the copper group.

7. Of the sulphides of the copper group none dissolve to a significant extent in the monosulphide. Considerable CuS (5 to 10 mgrms.) and a little HgS (0·5 to 1·0 mgrm.) may, however, dissolve in the polysulphide when the substance contains a large quantity of these elements. Yet when 2 mgrms. of either of these elements are present it can be detected in the analysis of the copper group, even when the polysulphide is used, provided only one treatment with it has been made.

8. Some sulphides, especially CdS, upon washing pass through the filter in the colloidal condition; the addition of a salt, such as NH_4NO_3, prevents this by coagulating the colloidal particles.

(To be continued)

OBITUARY.

GEORGE E. DAVIS.

We regret to announce the death on Saturday, April 20th, after a short illness, of Mr. George E. Davis, the founder and editor of the *Chemical Trade Journal*.

Mr. Davis was formerly one of Her late Majesty's Inspectors under the Alkali, &c., Works Regulation Acts; he was one of the original Fellows and subsequently a Member of Council of the Institute of Chemistry; a Fellow of the Chemical Society; and he took a prominent part in the inauguration of the Society of Chemical Industry, filling in succession the offices of Honorary Secretary, Member of Council, Chairman of the Manchester Section, and Vice-President.

Mr. Davis contributed largely to chemical, technological, and microscopical literature. His "Handbook of Chemical Engineering" was published in 1901, and his other collected works include "Sizing and Mildew in Cotton Goods" (written in conjunction with Dr. Dreyfus and Mr. Philip Holland, F.C.S.), "The River Irwell and its Tributaries" (of which he was co-author with his brother, Mr. Alfred R. Davis), and numerous other miscellaneous pamphlets, lectures, &c. From its commencement in 1887 he acted as Editor-in-Chief of the *Chemical Trade Journal*. Mr. Davis was in his fifty-seventh year.

Society of Chemical Industry.—Consideration of the Patents and Designs Bill, 1907.—On Friday next, May 10, a critical statement upon this Bill, prepared at the request of the Sectional Committee (London) by the Chairman and Honorary Secretary, will be communicated by the Chairman. A Discussion will follow.

Institute of Chemistry.—*Pass List of the April Examinations*, 1907.—Of seven candidates who entered for the Intermediate Examination, three passed: Eric Hayward, Herbert Mansfield, B.Sc. (Lond.), and C. J. H. Stock, B.Sc. (Dunelm). In the Final Examination for the Associateship (A.I.C), of three candidates examined in the branch of Mineral Chemistry, two passed: F. W. Foreman, and Robert Gillespie, Assoc.R.C.Sc (Lond.); of three in the branch of Metullurgical Chemistry, 2 passed: Edward Cahen, Assoc.R.C.Sc. (Lond.), and C. A. Wonham, BSc. (Lond.); of six in Organic Chemistry, five passed: E. R. Chrystall, B.Sc (Lond.), P. A. Houseman, Ph.D. (Würzburg), Edward Jones, B.Sc. (Wales), F. G. Shepheard, B.Sc. (Lond.), Assoc.R.C.Sc. (Lond), and J. M. Weir, M.A., B.Sc. (St. Andrews); and of six in the branch of the Analysis of Food and Drugs and of Water, including an examination in Therapeutics, Pharmacology, and Microscopy, the following three passed: W. M. Seaber, B.Sc (Lond.), H. L. Smith, B.Sc. (Manchester), and J. H. Totton, B.A., B.Sc. (R.U.I.).

Bismuth Iodide.—Lothar Birckenbach.—No method is known of preparing bismuth iodide in such a state of purity that it can be used for atomic weight determinations. If bismuth and iodine are fused together, the iodide always contains some metallic bismuth, and when prepared in the wet way it is never free from oxyiodide, nor can the perfectly pure substance be obtained by sublimation. If, however, a solution of stannous chloride in hydrochloric acid, saturated with hydrochloric acid gas, is saturated with iodine (which is very soluble in it), and bismuth oxide or oxychloride (in hydrochloric acid solution) is added, the iodide separates out in perfectly pure crystals. The crystals obtained by the author were drained, dried *in vacuo* over calcium chloride, and carefully heated in exhausted glass tubes to a temperature below the melting-point. Thus all impurities were volatilised, and the substance was then twice sublimed in a current of carbon dioxide and hydrogen. Analysis showed that the crystals were the pure iodide, BiI_3.—*Berichte*, xl., No. 6.

NOTICES OF BOOKS.

Physical Chemistry in the Service of Medicine. By Dr. WOLFGANG PAULI. Authorised Translation by Dr. MARTIN H. FISCHER. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

Dr. PAULI is well known as a pioneer in the investigation of the applications of physical chemistry to physiology and pathology, and his work has brought to light such valuable facts that English students of medicine who wish to keep themselves informed of the most recent work will find his book very interesting. The guiding thought which runs through these lectures is the close parallelism of changes in the colloidal state in vitro and in the living organism, and the author expounds more particularly the branch of physical chemistry dealing with energy relations. The fact that he most carefully refrains from stating too definitely as facts those observations which cannot yet be regarded as undoubtly correct makes the book very stimulating, while great originality is displayed in all the discussions of new methods and new points of view. The lectures are valuable both as giving a concise account of Dr. Pauli's own important work and also as providing excellent critical surveys of the comparatively few other investigations of the same branch of physical chemistry.

Practical Paper-making. By GEORGE CLAPPERTON. Second Edition. London: Crosby Lockwood and Son. 1907.

THIS book is above all things practical, tracing the process of paper-making straight through from the grading of the rags to the production of the finished article, and it may be safely said that every page reveals the hand of the paper-maker who has had wide experience and has made the utmost of his opportunities of forming opinions which will be of great value to his fellow manufacturers. As he writes more especially for mill owners and paper-makers, he rather slurs over the chemical knowledge which should be possessed by those who hope to pursue this industry to the greatest advantage, and for this reason the technical student would probably find that the book would require supplementing by one which went more fully into the theory of the chemical processes employed. However, methods of testing the chemicals to be used are given, and rough processes for detecting impurities in water, as well as tests for the ingredients of paper and outlines of the recovery of soda from waste liquors.

Vorträge uber die Entwicklungsgeschichte der Chemie von Lavoisier bis zur Gegenwart. ("Lectures on the History of the Development of Chemistry from Lavoisier to the Present Day"). By A. LADENBURG. Fourth Edition. Braunschweig: Friedrich Vieweg und Sohn. 1907.

IT is thirty-eight years since these lectures were first published, and scientific men everywhere will rejoice that Dr. Ladenburg has lived to revise them himself. Needless to say, this long period has seen very important and indeed fundamental developments in all branches of chemistry, which the author chronicles with all his accustomed vigour and vividness of expression. The first six lectures deal with inorganic and general chemistry, beginning with the phlogiston period; then the history of organic chemistry is taken up and treated very clearly, the author regarding it as practically without influence upon the early development of the science, and therefore best considered last. An additional lecture on the most important advances in the present century touches upon the discovery and investigation of radio-activity, the work of Werner upon valency, solid solutions, asymmetric nitrogen, &c., and in very short space gives clear accounts of the most striking points of each subject.

Anleitung für die Manipulationen bei den Barometrischen Höhenmessungen. ("Guide to the Manipulations in the Barometric Measurement of Altitudes"). By JOH. G. SCHOEN. Leipzig and Wien: Franz Deuticke. 1907.

THE author of this pamphlet has had occasion to take many measurements with mercury barometers, comparing the readings with those of aneroids, and now describes in considerable detail the results of his work, which extended over many years. He discusses first of all the choice of an instrument for various purposes, and explains the most convenient methods of transport and the precautions to be observed in moving all kinds of barometers. The taking of observations and application of corrections are fully described, together with the calculation of altitudes from barometric observations, and the pamphlet contains much useful information relating to barometric work in general.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 14, April 8, 1907.

The Nickel-tin Alloys.—Léon Guillet.—The author states that, in addition to the researches on the nickel-tin alloys published by M. Vigouroux, other important work has also been done on the same bodies by himself and others. He gives the following results of his own investigations:—Nickel and tin are capable of forming four solid solutions and one compound. A solution (α), magnetic, containing from 0 to 5 per cent tin; a solution (ε) containing the same amount of tin, but not magnetic; a solution (δ) containing 38 to 41 per cent tin; a solution (γ) containing 55 to 60 per cent tin; and, finally, the compound $NiSn$, consisting of beautiful crystals, visible to the naked eye. The alloys containing less than 38 per cent of tin are only magnetic at the ordinary temperature. All the alloys have transformation-points corresponding to the passage from the magnetic state to the non-magnetic. From the industrial point of view, only those alloys are of interest which form the two extremes, viz., those included in Solution α and those containing 65 per cent tin. These are ductile, and can be subjected to the same mechanical uses as nickel or tin, and possess greater ductility than either of the original metals.

Properties of the Alkaline Protoxides.—E. Rengade.—The alkaline protoxides, prepared in the manner previously described, but with the substitution of glass for the silver vessel used for oxidation and distillation of the alkali metal, present characteristic colorations. The oxides of rubidium, potassium, and sodium are less coloured than that of cæsium; that of rubidium is pale yellow cold, and golden yellow hot; that of potassium white at the ordinary temperature, yellow at 200°; that of sodium slightly yellowish when heated. Determination of the densities of these protoxides, taken in well-dried toluene and referred to water at 0°, gave the following results:—For sodium protoxide $d\ 0^{\circ} = 2{\cdot}25$; for potassium protoxide, 3·32; for rubidium protoxide, 3·72; for cæsium protoxide, 4·78. The protoxides of cæsium and rubidium, left standing at the ordinary temperature in the tube exhausted of air in which they were prepared, quickly changed in appearance; that of cæsium gradually lost its beautiful red colour and turned black; that of rubidium acquired a copper hue in parts. These colour changes do not occur if the oxides are heated *in vacuo* in a tube containing no alkali metal; and observation has shown that cæsium and rubidium possess a sensible vapour pressure at the ordinary temperature, and that these vapours are absorbed by the corresponding protoxides, though diffusion takes place only very slowly in the vacuum.

Research on the Oxybenzoates. — Œchsner de Coninck.—The author, with the object of ascertaining whether paroxybenzoic acid could be transformed into salicylic acid, investigated the action of heat upon barium paroxybenzoate. Prolonged heating at different temperatures produced no effect until 285° was reached. At this point there was still no formation of salicylic acid, but coloured substances soluble in ether were produced. One of these proved to be a barium carbonate derivative, evolving CO_2 when treated with acids:—

$$\left(C_6H_4{<}^{OH}_{CO_2}\right)_2Ba + 2H_2O = BaCO_3 + 2(C_6H_5OH) + CO_2 + H_2O.$$

If the paroxybenzoate is dry, containing no water of crystallisation, a basic salt, $C_6H_4{<}^{O}_{CO_2}{>}Ba$, is formed, and from this there is also a liberation of phenol and CO_2.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 5, 1907.

Experimental Proof of the Conditions for the Quantitative Equimolecular Transposition of Barium Chloride and Sodium Nitrite in Water.—J. Matuschek.—The author ground together dry barium chloride and sodium nitrite, and found that double decomposition takes place when the two substances are powdered and intimately mixed, and the quantitative decomposition of equimolecular weights of the two substances occurs in aqueous solution, provided that water is not present in excess. The yield of pure barium nitrite is very close to the theoretical yield if the amount of water used as solvent corresponds to only one-third of the calculated weight of the barium nitrite at 100°.

New Apparatus for Melting-point Determinations. —Johannes Thiele.—This consists of a tube of about 2 cm. diameter and length 12 cm., which is bent round in the form of a hgure 6, the curved part being connected with the middle of the tube, and having a diameter of 1 cm. The tube is filled with sulphuric acid, so that the upper mouth of the curved part is just closed by it, when the thermometer bulb is half way between the limbs of the curve. When the curved part is heated the sulphuric acid begins to circulate in the apparatus, moving from above downwards in the tube, and producing a very uniform rise in the thermometer reading. The apparatus is far more regular than any other form without a mechanical stirrer; it is heated very quickly, and cools again equally quickly, and is not more easily broken than other apparatus for determining melting-points. As the acid in the tube has a higher temperature above than below, the particles of substance in the upper part of the capillary fuse first, and thus it is easy to see when the neighbourhood of the melting-point has been reached.

Conditions of Fusel Oil Formation and their Connection with the production of Albumen by Yeast.—Felix Ehrlich.—The most important results of the author's work are as follows:—The formation of fusel oil in yeast fermentation is a consequence of the power of the living yeast cell to build up albumen, and proceeds in proportion as the yeast derives nitrogen from definite amino acids (especially leucine, isoleucine, and valine) during the fermentation of the sugar, and leaves behind the corresponding higher alcohols as indigestible metabolic products. From leucine in active isoamyl alcohol is formed from *d*-isoleucine *d*-amyl alcohol, and from valine isobutyl alcohol. The chief sources for the formation of fusel oil are the amino acids partly present as such in the natural maize, and partly split off from the albumen of the raw material. This follows from the fact that certain definite relations hold between the composition of the fusel oils and of the maize. The yield of fusel oil depends upon the amount of leucine present, as well as upon the amount and nature of the other compounds present. The largest quantities of amyl alcohol are obtained if leucine is fermented with pure sugar and pure yeast, poor in nitrogen, in absence of any other compound of nitrogen. By the addition of leucine and its homologues to fermenting maize the amount of fusel oil in the raw spirit can be increased, while the addition of other nitrogen compounds easily assimilated by the yeast would limit or altogether stop the formation of higher alcohols. The formation of fusel oil thus shows for the first time that a natural breaking down of the amino acids, connected with the building up of albumen, is the ordinary process in the life of yeast, and perhaps of other organisms.

Thermic Relations between Ozone, Nitric Oxide, and Hydrogen Peroxide. (III.).—Franz Fischer and Hans Marx.—The authors have continued their experiments on ozone formation with a Nernst pencil in liquid oxygen. An ozone-oxygen solution was obtained, the concentration of which always increased, though at a continually diminishing rate, with the duration of the experiment. The highest concentration amounted to 3·91 per cent of ozone in the liquid oxygen. The process must therefore be regarded as a concentration process. If highly ozonised air is blown on to Nernst pencils the degree of ozonisation is reduced. Hence it follows that only a small part of the air is in contact with the pencil, and is raised to a high temperature; otherwise the same ozonisation would be obtained whether ordinary or highly ionised air was used.

Acetyl Nitrate.—Amé Pictet and Eug. Khotinsky.—To prepare pure acetyl nitrate nitric acid anhydride (obtained by distilling concentrated nitric acid with phosphorus pentoxide) was dissolved in its own weight of acetic acid anhydride. No rise of temperature took place. The acetyl nitrate could be separated from the excess of acetic acid anhydride by fractional distillation under diminished pressure. At 22° and 70 mm. pressure it went over as a colourless mobile liquid which fumes in air. Its specific gravity is 1·24 at 15°. It attracts moisture energetically, and is decomposed by water instantaneously into its components, great heat being evolved. When strongly heated it explodes, and hence its composition cannot be determined by combustion. It was therefore analysed by dissolving in water, determining the total acid by titration and the nitric acid by Kjeldahl's method. It was thus found that the substance is the mixed anhydride of both acids, $CH_3.COO.NO_2$. Acetyl nitrate reacts violently with alcohol, forming the corresponding nitric acid ester and free acetic acid. It acts as an acetylating agent on amines, and nitrates aromatic compounds energetically, the equation being $R.H + CH_3.COO.NO_2 = R.NO_2 + CH_3.COOH$, and is a very convenient reagent to use for this purpose. Substances belonging to the fatty series, for example, chloroform, are also nitrated at higher temperatures. With acetic acid ethyl ester it yields a liquid which is insoluble in cold alkalis, and is saponified by alcoholic potash, forming the potassium salt of nitroform; this liquid is probably trinitro acetic ester.

Brucine Oxide.—Amé Pictet and G. Jenny.—Brucine like strychnine dissolves on gently warming in a 3 per cent solution of hydrogen peroxide. When the liquid cools colourless prisms of the oxide $C_{23}H_{26}N_2O_5 + 4\frac{1}{2}H_2O$ separate out. Brucine oxide containing water fuses at 124—125°, and the anhydrous substance at 199°, undergoing decomposition. It is soluble in alcohol and chloroform, insoluble in ether, petroleum ether, and benzene. It is taken up in the cold by water, forming an intensely bitter solution which is neutral to litmus and phenolphthalein. The colour reactions of the oxide (with nitric acid, stannous chloride, ammonium sulphide, sulphurous acid, potassium bichromate) are the same as those of brucine itself. It is converted into brucine by the action of sulphurous acid. It is a monatomic base, forming brucine oxide salts which are more soluble in water than those of

strychnine oxide. They are lævo-rotatory like the base itself, and are converted into brucine salts by reducing agents, such as sulphurous acid.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Society of Chemical Industry, 8. "The Works Chemist as Engineer," by O. Guttmann.
—— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 7th.—Royal Institution, 3. "Stimulatioo, Luminous and Chemical," by Prof. William Stirling, M.D., &c.
WEDNESDAY, 8th.—Society of Arts, 8. "The Production of Coke and its Application in Domestic Fires," by Paul Schlicht.
THURSDAY, 9th.—Royal Institution, 3. "Spectroscopic Phenomena in Stars," by H. F. Newall, F.R.S., &c.
FRIDAY, 10th.—Royal Institution, 9. "Recent Excavations on the Forum Romanum and the Forum Ulpium," by Signor Come Giacomo Boni.
—— Society of Chemical Industry, 8. Critical Statement upon, and Discussion of, "The Patents and Designs Bill, 1907."
—— Physical, 8. Stereoscopy with Long Base-line Illustrated on the Screen, by T. C. Porter.
SATURDAY, 11th.—Royal Institution, 3. "Scientific Work in the Sea Fisheries," by Prof. W. C. McIntosh.

ERRATUM.—P. 193, col. 2, line 32, *for* "may not give" *read* "may give."

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THE CHEMICAL NEWS.

Vol. XCV., No. 2476.

FOURTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS.

DETERMINATIONS PUBLISHED DURING 1906.*

By F. W. CLARKE.

(Concluded from p. 210).

Copper.

In order to determine the atomic weight of copper, Murmann (*Monatsh.*, xxvii., 351) made a series of experiments upon the oxidation of the metal by prolonged heating in a stream of air, followed by a series of reductions in hydrogen of the oxide so formed. His results range from Cu = 63·513 to Cu = 64·397, and are therefore too discordant to have much significance. The best determinations ran from 63·513 to 63·560, the value 63·53 being regarded by Murmann as the most probable. The individual data are given so confusedly that it is not desirable to attempt their reproduction here.

Cadmium.

The paper on cadmium by Baxter, Hines, and Frevert (*Journ. Am. Chem. Soc.*, xxviii., 770) is a continuation of a research which was published last year. Analysis of the bromide gave the following results when Ag = 107·93 and Br = 79·955 :—

Weight $CdBr_2$.	Weight AgBr.	Weight Ag.	Atomic weight Cd. AgBr ratio.	Atomic weight Cd. Ag ratio.
11·46216	15·81319	9·08379	112·466	112·468
6·82282	9·41267	5·40724	112·469	112·461
6·75420	9·31830	5·35277	112·460	112·465
7·08888	9·77649	5·61597	*112·444	*112·449
5·13859	7·08933	4·07226	112·461	112·473
5·84324	8·06130	4·63072	112·467	112·471
5·99704	8·27360	4·75259	112·463	112·472
5·90796	8·15070	4·68200	112·463	112·472
Mean, rejecting the starred values ..			112·464	112·467

New analyses of the chloride gave data as follows, when Cl = 35·473.

Weight $CdCl_2$.	Weight AgCl.	Weight Ag.	Atomic weight Cd. AgCl ratio	Atomic weight Cd. Ag ratio.
5·62500	—	6·61193	—	112·472
6·81031	10·64918	8·01496	112·471	112·470
5·50089	8·60174	6·47393	112·469	112·470
6·11750	9·56590	—	112·470	—
Mean			112·470	112·471

The final conclusion is that Cd = 112·47. All weights were reduced to a vacuum.

Tellurium.

The investigation by Norris (*Journ. Am. Chem. Soc.*, xxviii., 1675) was primarily to determine the definiteness of tellurium as an element by fractional processes which would prove the presence or absence of any other substance, such as the hypothetical "dvitellurium" of Mendeleeff. The integrity of the element having been established, the atomic weight determinations followed. The basic nitrate, $2TeO_2.HNO_3$, dried at 140° in a current of dry air, was decomposed by heating gradually, at last to 400—450°. The weights thus obtained are given below. The atomic weight, reduced to a vacuum standard, was computed with H = 1·0076 and N = 14·01.

Weight nitrate.	Weight TeO_2.	Atomic weight Te.
2·28215	1·90578	127·47
2·35429	1·96615	127·53
1·86853	1·56042	127·49
1·77348	1·48110	127·49
2·31048	1·92938	127·44
2·14267	1·78936	127·50
2·35523	1·96676	127·45
2·18860	1·82780	127·54
3·29158	2·74881	127·50
2·27516	1·89993	127·46
2·53164	2·11410	127·46
2·01327	1·68121	127·45
Mean		127·48

Without reduction to vacuum and with N = 14·04, Te = 127·64. Kothner, under these conditions, found Te = 127·63, and his data, reduced, became Te = 127·47. The two series of determinations are therefore in good accord, but differ materially from recent measurements by other methods, which agree in making Te = 127·60. The cause of this difference is unexplained.

Bismuth.

In the report for 1905, a dissertation by Birckenbach was noticed, which contained determinations of atomic weight made under the direction of Gutbier at Erlangen. Two more dissertations from the same laboratory have since appeared, giving additional determinations by other methods.

Mehler determined the ratio between bismuth bromide and silver bromide (Doctoral Dissertation, Erlangen, 1905). The results obtained, with vacuum weights, are subjoined. The computation was based upon Br = 79·96, Ag = 107·934.

Weight $BiBr_3$.	Weight AgBr.	Atomic weight Bi.
3·77071	4·74323	208·24
4·37676	5·50932	207·92
8·64088	4·58160	208·05
4·57894	5·76183	208·08
4·53204	5·70410	208·89
2·85054	3·58682	208·10
4·58310	5·76618	208·14
6·47910	8·15465	207·99
Mean		208·05

In the other investigation, by Janssen (Doctoral Dissertation, Erlangen, 1906), the synthesis of bismuth sulphate from the metal was effected. The metal was first dissolved in nitric acid, and then treated with sulphuric acid, with various precautions which cannot be discussed here. The final data are as follows, reduced with S = 32·06 :—

Weight Bi.	Weight sulphate.	Atomic weight Bi.
2·4045	4·0706	207·951
2·41900	4·09445	208·040
2·20280	3·72745	208·178
2·57206	4·35444	207·928
5·79241	9·79987	208·266
3·65233	6·18143	208·082
Mean		208·074

Although the data given by Mehler and Janssen are by no means sharply concordant, they corroborate the results obtained by Birckenbach, and agree with the earlier determinations of Löwe, Schneider, and Marignac. For practical purposes the even value Bi = 208 may be employed.

Palladium.

In order to determine the atomic weight of palladium, Krell (Doctoral Dissertation, Erlangen, 1906) reduced weighed quantities of palladosamine chloride, $PdN_2H_6Cl_2$, by heating in hydrogen. The reduced palladium was

* From the *Journal of the American Chemical Society*, xxix., No. 3.

afterwards heated in a stream of carbon dioxide, in order to free it from occluded hydrogen. The data given are as follows, with vacuum weights:—

Weight chloride.	Weight Pd.	Per cent Pd.	Atomic weight Pd.
1·83034	0·92197	50·372	106·59
1·73474	0·87433	50·401	106·72
1·92532	0·96524	50·396	106·72
2·63544	1·32868	50·416	106·78
3·23840	1·63175	50·387	106·66
		Mean	106·694

If the first experiment is rejected, this becomes 106·72. The atomic weights used were those of the International Committee for 1906.

Tantalum.

Hinrichsen and Sahlbom (*Ber.*, xxxix., 2600) have determined the atomic weight of tantalum by oxidising the metal to pentoxide. The metal was obtained from Siemens and Halske, and contained no appreciable impurity. The oxidation was effected by direct heating in oxygen. The results obtained, with vacuum weights and with O = 16, were as follows:—

Weight Ta.	Weigbt Ta_2O_5.	Atomic weight Ta.
0·37200	0·45437	180·65
0·41278	0·50364	181·77
0·33558	0·40975	180·98
0·35883	0·43807	181·14
0·47554	0·58087	180·59
	Mean	181·03

From the sum of the weights the authors deduce Ta = 180·98, or 181 in round numbers. Potassium tantalifluoride was investigated and found to be unsuitable for good atomic weight determinations.

THE RARE EARTHS.

During 1906 an unusual number of determinations have been published relative to the atomic weights of the rare earth metals. First, Urbain (*Comptes Rendus*, cxlii., 957) has made a good determination of the atomic weight of terbium by estimating the amount of water in the octohydrated sulphate. The amount of oxide was not determined because the product obtained on igniting the sulphate varied in composition. The data are subjoined:—

Weight octohydrate.	Anhydrous sulphate.	Atomic weight Tb.
2·0407	1·6489	159·20
1·9626	1·5859	159·30
2·2580	1·8245	159·19
2·2385	1·8087	159·17
2·0037	1·6190	159·19
	Mean	159·22

Calculated with H = 1·007 and S = 32·06. Hinrichs, rediscussing these data, argues in favour of Tb = 159 (*Comptes Rendus*, cxliii., 1196).

Two series of determinations by Urbain and Demenitroux relate to dysprosium (*Comptes Rendus*, cxliii., 598; preliminary in cxlii., 727). They represent different fractions of the material studied, and were obtained by the ignition of the octohydrated sulphate.

First Series.

Weight sulphate.	Weight Dy_2O_3.	Atomic weight Dy.
1·1966	0·8359	162·61
2·0926	1·0301	162·29
1·8415	0·9069	162·45
1·5519	0·7649	162·75
2·4955	1·2296	162·64
1·8130	0·8927	162·39
	Mean	162·52

Second Series.

Weight sulphate.	Weight Dy_2O_3.	Atomic weight Dy.
1·8817	0·9271	162·61
1·1164	0·5500	162·59
1·7308	0·8528	162·63
2·6038	1·2820	162·36
1·6942	0·8346	162·56
2·1776	1·0726	162·52
	Mean	162·54

This paper was followed by a communication from Hinrichs, who attempts to show that Dy = 162·5 exactly (*Comptes Rendus*, cxliii., 1143).

O. Holmberg, in a doctoral dissertation (*Akademisk Afhandling, Upsala*, 1906), has given a series of determinations of the atomic weight of neodymium. The data, representing syntheses of the sulphate from the oxide, are subjoined:—

Weight Nd_2O_3.	Weight $Nd_2(SO_4)_3$.	Atomic weight Nd.
0·9692	1·6618	144·05
0·6584	1·1287	144·12
1·0292	1·7643	144·13
1·0118	1·7346	144·10
0·5518	0·9462	144·01
0·5345	0·9164	144·07
	Mean	144·08

Feit and Przibylla, by a special volumetric method, have re-determined the atomic weights of several rare earth metals (*Zeit. Anorg. Chem.*, l., 249). The oxides were dissolved in definite weighed quantities of half-normal sulphuric acid, and the slight excess of the latter was determined by titration with a decinormal solution of sodium carbonate. From the amount of acid required to form neutral salts, the authors compute the amount of oxygen in the oxides, and thence deduce the atomic weight of the elements. The data, somewhat condensed from the original, are as follows:—

Lanthanum.

Weight La_2O_3.	Oxygen.	Atomic weight La.
0·5125	0·07544	139·05
0·5256	0·07731	139·11
0·4835	0·07116	139·08
0·5235	0·07706	139·04
0·4815	0·07088	139·03
0·5156	0·07585	139·15
0·5348	0·07867	139·15
	Mean	139·09

Reduced to a vacuum standard, La = 139·17.

Praseodymium.

Weight Pr_2O_3.	Oxygen.	Atomic weight Pr.
0·54010	0·07879	140·51
0·53240	0·07789	140·60
0·50054	0·07302	140·51
	Mean	140·54
	With vacuum weights ..	140·62

Neodymium.

Weight Nd_2O_3.	Oxygen.	Atomic weight Nd.
0·5380	0·07661	144·54
0·5388	0·07675	144·48
0·5358	0·07632	144·49
0·5265	0·07497	144·56
	Mean	144·52
	With vacuum weights ..	144·60

Samarium.

Weight Sa_2O_3.	Oxygen.	Atomic weight Sa.
0·5576	0·07668	150·53
0·5576	0·07670	150·47
0·5583	0·07684	150·38
0·5633	0·07747	150·51
	Mean	150·47
	With vacuum weights ..	150·56

Europium.

Weight Eu_2O_3.	Oxygen.	Atomic weight Eu.
0·3961	0·05835	152·54
0·4096	0·05566	152·62
0·4115	0·05594	152·56
	Mean	152·57
	With vacuum weights ..	152·66

Gadolinium.

Weight Gd_2O_3.	Oxygen.	Atomic weight Gd.
0·3852	0·05097	157·37
0·3956	0·05234	157·40
	Mean	157·38
	With vacuum weights ..	157·17

Ytterbium.

Weight Yb_2O_3.	Oxygen.	Atomic weight Yb.
0·6424	0·07808	173·46
0·6408	0·07783	173·60
0·6403	0·07779	173·55
0·6466	0·07858	173·48
	Mean	173·52
	With vacuum weights ..	173·52

Yttrium.

Two sets of determinations were made on two different preparations. They are here treated as one.

Weight Yt_2O_3.	Oxygen.	Atomic weight Yt.
0·3677	0·07781	89·42
0·4928	0·10438	89·31
0·3660	0·07749	89·36
0·3660	0·07751	89·33
0·3704	0·07840	89·39
0·3635	0·07701	89·29
	Mean	89·35
	With vacuum weights ..	89·40

In Abegg's "Handbuch der Anorganischen Chemie" a series of excellent summaries of atomic weight determinations, written by Brauner, has appeared. In the sections relative to the rare earth metals (Band 3, Abth. 1, pp. 263, 276, 284, 304, 318, 335) Brauner gives some previously unpublished data of his own, which can be briefly summarised as follows :—

Praseodymium.

Atomic weight determined by four methods.

First, reduction of the octohydrated sulphate to oxide.

Weight sulphate.	Weight oxide.	Atomic weight Pr.
1·29269	0·59747	141·13
1·27990	0·59137	141·04
	Mean	141·09

Second, analysis of the anhydrous sulphate.

1·03242	0·59747	140·96
1·02193	0·59137	140·94
	Mean	140·95

Third, synthesis of the sulphate from the oxide.

1·26782	0·73359	140·91
0·12059	0·64871	141·09
1·28051	0·74103	140·96
1·25792	0·72894	140·92
0·63350	0·36559	140·94
1·43024	0·82769	140·96
	Mean	140·96

Fourth, analysis of the oxalate. The Pr_2O_3 in each sample of the oxalate was determined, and also, volumetrically, by titration with potassium permanganate, the amount of C_2O_3. The *mean* results are given below for four different samples of oxalate.

Per cent Pr_2O_3.	Per cent C_2O_3.	Atomic weight Pr.
45·183	29·581	140·96
45·090	25·517	140·98
45·0775	29·493	141·07
45·136	29·5635	140·89
	Mean	140·98

Brauner regards Pr = 140·96 as the best value for Pr, which may be rounded off to 141·0.

Neodymium.

Three syntheses of the sulphate are given, from different samples of the oxide. The last one, which Brauner regards as trustworthy, is as follows :—

0·93788 grm. Nd_2O_3 gave 1·60873 $Nd_2(SO_4)_3$. Hence Nd = 143·89.

Samarium.

Analysis of the sulphate.

1·36567 grm. $Sa_2(SO_4)_3.8H_2O$ gave 1·09770 $Sa_2(SO_4)_3$. Sa = 150·76.

1·09770 $Sa_2(SO_4)_3$ gave 0·65046 Sa_2O_3. Sa = 150·66. Mean, 150·71.

As the material was not entirely free from europium this value is too high.

Gadolinium.

0·88884 Gd_2O_3 gave 1·48257 $Gd_2(SO_4)_3$ and 1·83903 $Gd_2(SO_4)_3.8H_2O$. Hence, Gd = 155·78, which is somewhat too low.

Erbium.

1·09395 Er_2O_3 gave 2·53997 $Er_2(SO_4)_3$. Er = 167·14.

Ytterbium.

1·067279 Yb_2O_3 gave 2·69209 $Yb_2(SO_4)_3$. Yb = 173·08.

Baxter and Griffin (*Journ. Am. Chem. Soc.*, xxviii., 1684) have shown that the oxalates of the rare earths, under certain conditions, carry down ammonium oxalate. This possibility should be borne in mind in any determination of atomic weights by the oxalate method.

Wyrouboff and Verneuil, in a long paper upon cerium (*Ann. Chim. Phys.*, [8], ix., 349), reproduce their determinations of 1897, and defend them against criticisms. No new determinations are given.

Some additional information upon thorium, berzelium, and carolinium has been published by Baskerville ("Fourth Annual Report Carnegie Institution," p. 136; and Fifth Report, p. 144). The report is one of progress, without final results.

Miscellaneous Notes.

Bradbury (Chemical News, xciv., 157 and 245) has pointed out certain relations between the atomic weights of several elements, but his results do not seem to have any great importance. There is also a memoir by Hinrichs, in which he reiterates his well-known views in favour of whole number atomic weights and criticises the modern determinations (*Chem. Cent.*, 1906, i., 197; abstract from the *Moniteur Scientifique*, which I have not seen).

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART II.—ANALYSIS OF THE SILVER, COPPER, AND TIN GROUPS.

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 213).

PROCEDURES AND NOTES (*continued*).

Analysis of the Copper Group.

Procedure 23.—To the residue from the ammonium sulphide treatment (P. 22) in a casserole add 10 to 20 cc. of a mixture of one volume HNO_3 (1·20) and two volumes water, heat to boiling, and boil gently for a minute or two. (Black residue, possible presence of *mercury*). Filter and wash. (Residue, P. 24; solution, P. 26).

Notes.

1. Boiling HNO_3 of this concentration dissolves the sulphides of lead, bismuth, copper, and cadmium almost immediately, and is therefore preferable to a more dilute acid, with which the reaction would require for its completion several minutes' boiling. Scarcely any HgS is dissolved by the above treatment, unless the boiling is long continued.

2. Moderately concentrated HNO_3 dissolves sulphides much more rapidly than HCl or H_2SO_4 of the same concentration; for with the latter acids the sulphide ion is removed from the solution only by combination with the hydrogen ion forming slightly ionised H_2S and by the volatilisation of the latter, while with HNO_3 the sulphide ion (or the H_2S in equilibrium with it) may also be destroyed by oxidation to ordinary sulphur. The oxidising effect of HNO_3 is, however, considerable only when it is hot and moderately concentrated.

3. That HgS, unlike the other sulphides, does not dissolve in the dilute HNO_3 is doubtless due to the much smaller concentration of its ions in its saturated solution and to the fact that at this small concentration the sulphide ion (or the H_2S in equilibrium with it at a correspondingly small concentration) is oxidised only very slowly by the dilute HNO_3. HgS is, however, readily dissolved by more vigorous oxidising agents, such as aqua regia or bromine water, since they react rapidly with sulphide ion (or with H_2S) even when its concentration is very small.

4. If more concentrated HNO_3 be used, or if the acid become concentrated by long boiling, the black HgS is dissolved in part, and the remainder is converted into a heavy, white, difficultly soluble compound, $Hg(NO_3)_2.2HgS$.

5. When much lead, copper, or bismuth is present the sulphur formed will generally enclose enough of the undissolved sulphide to give it a black colour. [*Moreover, PtS_2 and Au or Au_2S, if present, are not dissolved by the HNO_3. A black residue is therefore not necessarily HgS, and must be further tested for mercury as described in P. 24.

6. Some sulphur is always oxidised to H_2SO_4 by the boiling HNO_3, but, even in the presence of much lead, $PbSO_4$ is not precipitated, owing to its moderate solubility in HNO_3.

7. Any SnS or SnS_2 not extracted by the ammonium sulphide treatment will be converted by HNO_3 into metastannic acid, most of which remains undissolved. Therefore even a light coloured residue must be carefully collected if tin is to be tested for in this group.

Procedure 24.—Transfer the residue undissolved by HNO_3 (P. 23), with the filter if necessary, to a casserole, add 10 to 40 cc. saturated Br_2 solution, cover the dish, and warm slightly for five to ten minutes, with frequent stirring. Boil the mixture until the bromine is expelled, and filter. (Residue, P. 25). [*If the solution is yellow, indicating that gold or platinum may be present, treat it by *P. 24*a*, and then proceed as follows]:—Cool the solution, and add to it a few drops of HCl (1·12) and a 2 per cent $SnCl_2$ solution, at first drop by drop; then add several cc. of a 10 per cent $SnCl_2$ solution. (White precipitate turning grey, or grey precipitate, presence of *mercury*). (Residue and solution, reject.

Notes.

1. Bromine water dissolves the sulphides of mercury, platinum, and gold, but leaves in the residue any metastannic acid. In case tin need not be tested for at this point, the residue may be more quickly dissolved by warming it with HCl (1·12), and adding gradually a little solid $KClO_3$; since metastannic acid is soluble in HCl, this then passes into solution with the mercuric salt.

2. In the final test for mercury HCl is added to prevent the precipitation of a basic tin salt when the $SnCl_2$ reagent is diluted, and to cause the formation at first of white Hg_2Br_2 or Hg_2Cl_2. For the latter reason, also, dilute $SnCl_2$ solution is added drop by drop to the cold solution. By the excess of $SnCl_2$ the white precipitate is reduced to grey finely divided mercury.

3. The presence of mercury at this point does not show that it was originally in the mercuric state, except in case the substance was dissolved without the use of hot or concentrated HNO_3. If it is desired to determine in which state the mercury was originally present, a solution of the substance in water, in dilute H_2SO_4, or in cold very dilute HNO_3, must be prepared and analysed for mercurous and mercuric mercury by the regular process, beginning with P. 11.

*4. Platinum and gold compounds, if not remove l, are reduced by $SnCl_2$, the former giving a reddish brown solution and the latter a dark coloured or purple precipitate of metallic gold. The presence of these elements would thus interfere with, or prevent the detection of, mercury, and it is therefore directed to remove them.

**Procedure* 24*a*.—To the solution of the sulphides in bromine water (P. 24) add about 0·5 grm. solid KCl and 1 to 2 cc. HCl (1·12), evaporate until KCl crystallises out, cool, and add water drop by drop until almost all the KCl has dissolved. (Yellow precipitate, presence of *platinum*). Filter and wash with a little saturated KCl solution. Confirm the presence of platinum in the precipitate by *P 43*a*. To the filtrate add 10 per cent NaOH solution till alkaline, and then about 1 cc. more. Then add saturated oxalic acid ($H_2C_2O_4$) solution until the solution becomes distinctly acid, dilute to about 15 cc., and digest on a steam-bath for ten to fifteen minutes. (Purplish black or dark yellow precipitate, presence of *gold*). Filter. Reject the precipitate. Test the filtrate for mercury with $SnCl_2$ solution by the last part of P. 24.

Note.

1. For notes upon this process, see under *P 43*a* and 43*b*. By means of it can be detected 1 mgrm. of gold or platinum in the presence of much mercury (at least 200 mgrms.), or 1 mgrm. of mercury in the presence of much gold or platinum.

Procedure 25.—If it is necessary to extract tin (see N. 1 below) from the residue undissolved by HNO_3 and bromine water (P. 24), digest it, if it is still dark coloured, with another portion of bromine water to extract the rest of the mercury, filter, reject the filtrate, and warm the residue slightly with 2 to 5 cc. ammonium monosulphide, filter, and unite the solution with the main ammonium sulphide solution obtained in P. 22.

Note.

1. If it is desired to detect with certainty the presence in the substance of a quantity of tin smaller than 5 mgrms., and if the elements of the copper group are

* From the *Technology Quarterly*, xix., No. 3, September, 1906.

present in large quantity (100 to 500 mgrms.), it is necessary to recover the tin that remained with the copper group; for, as stated in P. 22, N. 5, a quantity of tin as large as 5 mgrms. (or even larger when stannous tin and cadmium are both present) may remain entirely in the residue undissolved by ammonium sulphide when this residue is large. By extracting the tin as described in this procedure and uniting it with the main solution of the tin group 2 mgrms. of tin can be detected.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 22nd, 1907.

Prof. R. Meldola, F.R.S., President, in the Chair.

Dr. G. D. Lander and Dr. J. F. Thorpe were appointed scrutators, and the Ballot was opened for the election of Officers and Council for the ensuing year.

The President presented the Report of the Council on the progress of the Society during the past twelve months. The adoption of the Report of the Council was proposed by Prof. J. B. Harrison, seconded by Prof. W. Jackson Pope, and carried unanimously.

Report of the Council.

The Council has the satisfaction of being able to report the continued prosperity of the Society, and that, measured by the number of papers read and the number of Fellows on the list, there has been greater activity than in any previous year.

On December 31st, 1905, the number of Fellows was 2785. During 1906, 172 Fellows were elected, and 2 reinstated, thus making a gross total of 2959. The Society has lost 24 Fellows by death; 24 have resigned, the elections of 5 have become void; 39 have been removed for non-payment of Annual Subscriptions, and 7 Life Compounders, whose addresses could not be found, have been removed.

The total number of Fellows, therefore, on December 31st, 1906, was 2860, showing an increase of 75 over the number for the previous year.

The names of the deceased Fellows, with the dates of their election, are:—W. H. Chandler (1872), F. J. Claudet (1852), T. S. Davis (1876), W. H. Edwards (1902), M. H. Foye (1884), C. H. B. Hambly (1859), J. G. Hepburn (1853), J. S. C. Heywood (1848), G. H. Hurst (1885), F. M. Lyte (1859), C. W. Marsh (1881), E. H. Miller (1897), W. J. Orsman (1884), B. Phillips (1889), J. E. Pitman (1906), T. Royle (1862), F. Smith (1890), T. D. Smith (1893), H. J. P. Sprengel (1864), W. S. Squire (1858), J. A. Storey (1891), C. Tookey (1855), T. B. Tyson (1885), Maj.-Gen. A. Walker (1868).

The number of the Fellows who were elected in the early part of the last century has been still further diminished by the death of Mr. F. J. Claudet, elected on February 16th, 1852; Mr. J. G. Hepburn, elected on February 21st, 1853; and of Mr. J. S. C. Heywood, who was elected on April 3rd, 1848.

The number of Honorary and Foreign Members at the close of 1905 was 34. No elections have been held during 1906, but the Society has to mourn the loss of Dr. Fedor Beilstein, who was elected February 1st, 1883, and who died on October 19th, 1906. The number of Honorary and Foreign Members at December 31st, 1906, was therefore 33.

Since the close of 1906, the Society has lost by death three more of its Honorary and Foreign Members, namely, Prof. Dr. D. I. Mendeleeff (on February 2nd), Prof. Dr. Nicolai Menschutkin (on February 4th), and Prof. Henri Moissan (on February 20th).

During the year 1906, 236 scientific communications have been made to the Society, 176 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1906 contains 1943 pages, of which 1890 are occupied by 186 memoirs, the remaining 53 pages being devoted to the Cleve Memorial Lecture, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 184 memoirs, which occupy 1818 pages.

The Journal for 1906 contains also 4541 abstracts of papers, published mainly in foreign journals, which extend to 1912 pages, whilst the abstracts for 1905 numbered 4356, and occupied 1828 pages.

The abstracts for 1906 may be classified as follows:—

	Pages.	No. of Abstracts.
Part I.		
Organic Chemistry	1000	1745
Part II.		
General and Physical Chemistry ..		651
Inorganic Chemistry..		559
Mineralogical Chemistry..		128
Physiological Chemistry		486
Chemistry of Vegetable Physiology and Agriculture		343
Analytical Chemistry		629
	912	2796
Total in Parts I. and II. ..	1912	4541

Among the first acts of the Council elected in March, 1906, was the appointment of a Finance Committee, and it was decided also that the names of the Members, together with those of the House, Library, Publication, and Research Fund Committees, should be read from the Chair at the Ordinary Meeting next after the Meeting of Council at which the Committees are formed.

In the previous Session, and on a second occasion during the present one, the desirability of reading the minutes at an Ordinary Meeting has been called in question; for the guidance of Chairmen on this point it has been resolved that henceforth the minutes must be read as long as the present by-laws remain in force.

The practice of holding the Ordinary Meetings of the Society on the first and third Thursdays of the month, reversion to which was announced in the last Annual Report, appears justified by the average attendance of Fellows, which has been well maintained. In order to relieve the pressure of business which has been usual at the first and last Meetings of the Session, it was decided to hold two extra Meetings, in October and July respectively.

The triennial award of the Longstaff Medal to the Fellow of the Society who, in the opinion of the Council, has done the most to promote Chemical Science by Research, was made, on the recommendation of the Research Fund Committee, to Prof. Walter Noel Hartley, F.R.S., in recognition of his spectrochemical investigations. The medal was presented on October 18th, 1906.

On the occasion of the International Celebration marking the Fiftieth Anniversary of the Foundation of the Coal-tar Colour Industry, an Address of congratulation to Sir William Henry Perkin, F.R.S., was presented on behalf of the Society by the President. In accordance with the resolution of the public meeting at which the commemoration was inaugurated, a marble bust of Sir William Perkin, executed by Mr. F. W. Pomeroy, A.R.A., has been presented to the Society by the Committee administering the Fund subscribed in support of the celebration.

The Society has also received a Berzelius medal cast in selenium, presented by Mr. John Spiller, and Prof. J. M. Thomson, F.R.S., has presented an aqua-tint engraving of Dr. Thomas Thomson, F.R.S., Regius Professor of Chemistry in the University of Glasgow from 1818 to 1852.

During the vacation of 1906 an Address was presented to the University of Aberdeen at the celebration of its Fourth Centenary, which took place in September. The congratulations of the Society were offered also to the distinguished Honorary and Foreign Member, Prof. Adolph Lieben, on the occasion of his seventieth birthday and fiftieth anniversary of his doctorate.

The desirability of applying for a supplemental Charter with a view to removing existing restrictions in regard to nationality and sex as affecting election to the Fellowship of the Society has been carefully considered by the Council. After receiving the report of a Special Committee, consisting of Mr. Phipson Beale, Mr. Bousfield, Dr. Horace Brown, Dr. Moody, Prof. Emerson Reynolds, Dr. T. E. Thorpe, Prof. W. A. Tilden, and the Officers, the Council resolved that for the guidance of Chairmen, only those Fellows who are British subjects can vote at meetings or be eligible for offices, and that the matter be made clear by adding to the gloss on the Charter, after the first paragraph, the words "but British subjects who are Fellows can alone exercise corporate rights, or be eligible for office."

The Council has resolved that, following the ordinary index of the *Transactions*, there shall appear a list of new compounds described in the original communications, tabulated according to the Richter system.

The alchemical and early chemical works presented to the Library by Sir Henry E. Roscoe have been catalogued (*Proc.*, 1906, xxii., 209—233), and the volumes placed in a special book-case.

The number of books borrowed from the Library during 1906 was 1126, as against 1108 in the previous year. The additions to the Library comprise—(*a*) a collection of 136 alchemical and other books presented by Sir Henry E. Roscoe; (*b*) 121 books, of which 64 were presented, 385 volumes of periodicals, and 32 pamphlets, as against 165 books, 324 volumes of periodicals, and 48 pamphlets last year.

In January last the Council decided that during the remainder of the present Session the Library shall be kept open for the use of Fellows every Thursday from 10 a.m. until 9 p.m., except on those evenings on which the Society meets, when it will remain open until 10.30 p.m.

The annual income of the Research Fund from its investments is £219 17s., and from this grants amounting to £210, as well as the Longstaff Honorarium and Medal, had to be paid. That this should be not only possible, but that there should also be an excess of income over expenditure of £26 13s. 11d. for the year, is due to the amount of £38 6s. 11d. having been returned from grants made in previous years. In the *Transactions* for 1906 there are 31 papers contributed by authors to whom grants had been made from the Research Fund.

The Treasurer has great pleasure in recording that in February of the present year the Society received a further munificent donation of £1000 to the Research Fund from the Worshipful Company of Goldsmiths. The income accruing from this donation will, in accordance with the expressed wish of the donors, be devoted especially to the encouragement of research in metallurgy and inorganic chemistry.

The financial transactions of the Society for the past year have been very satisfactory, and show a substantial surplus. The total income of the Society for 1906 is £7121 8s. 11d., being an increase of £327 14s. 11d. over that for 1905 (£6793 14s.) in spite of the fact that the amount received on account of Life Composition Fees has fallen from £360 to £268, a decrease of £92. The increase in income is mainly composed of the following three items: —(1) Admission fees, £120; (2) annual subscriptions, £138 18s.; and (3) sale of publications, £120 6s. 3d. Whilst the income has notably increased, the expenditure has fallen much more considerably, and is £718 19s. 8d. less than last year, so that instead of a deficit of £305 1s. 5d. on the year's working there is a surplus of £741 13s. 2d., a difference in all of £1046 14s. 7d. This is due very largely to having no expenses of any kind to meet on account of the Collective Index, which last year alone cost the Society £778 10s. 5d., but it must not be thought that nothing is being done towards the preparation of the next volume, because the card indexes now made by Mrs. Dougal for each Annual Index will, with comparative little expense and labour, be blended together and thus utilised for the preparation of Vol. V. of the Collective Index, which will cover the period 1903-1912.

The cost of the *Journal*, the *Proceedings*, and the *Annual Reports* all show increased expenditure, amounting to £71 7s. 6d., £40 6s., and £68 10s. 7d. respectively. It is very satisfactory to notice that although the *Transactions* and *Abstracts* show an increase of over 200 pages and contain several lengthy, as well as important and expensive, papers, the increase in cost should be so small. In this connection the Treasurer has to thank Prof. Pope and Mr. Barlow for supplying all the blocks required to illustrate their paper published in the November issue of the *Journal*. The increased cost of the *Proceedings* is due in part to the issue of two additional numbers corresponding to the two extra meetings of the Society in July and in October, and in part also to the printing of the catalogue, compiled with great care by the Librarian, of the collection of alchemical works above referred to which the Society owes to the generosity of Sir H. E. Roscoe, and which are now properly housed in the Library.

The balance sheet also shows that a small legacy of £33 12s. 3d. has been received under the will of the late Mr. Henry Dircks, and is a residue of the estate from which almost exactly thirty years ago the Society received £840 5s.

The TREASURER gave a statement as to the Society's Income and Expenditure during the year 1906, and proposed a vote of thanks to the Auditors, which was seconded by Dr. W. R. E. HODGKINSON and carried unanimously. Acknowledgment was made by Mr. E. GRANT HOOPER.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Sir WILLIAM H. PERKIN, seconded by Dr. E. DIVERS, and adopted unanimously; this was acknowledged by Sir WILLIAM RAMSAY.

The PRESIDENT then delivered his Address, entitled "The Position and Prospects of Chemical Research in Great Britain. Dr. T. E. THORPE proposed a vote of thanks to the President coupled with the request that he would allow it to be printed in the Society's *Transactions*.

The motion was seconded by Prof. J. MILLAR THOMSON and carried with acclamation, the PRESIDENT making acknowledgment.

The Scrutators then presented their Report to the Chairman, who declared that the following had been duly elected as Officers and Council for the ensuing year:—

President—Sir William Ramsay, K.C.B., F.R.S.

Vice-Presidents who have filled the office of President—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; Sir W. H. Perkin, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents—J. J. Dobbie, M.A., D.Sc., F.R.S.; Rudolph Messel, Ph.D.; Sir Alexander Pedler, C.I.E., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; A. Smithells, B.Sc., F.R.S.; W. P. Wynne, D.Sc., F.R.S.

Treasurer—Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries—M. O. Forster, D.Sc., Ph.D., F.R.S.; A.W. Crossley, D.Sc., Ph.D.

Foreign Secretary—Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council—Edward C. C. Baly; George T. Beilby, F.R.S.; Bernard Dyer, D.Sc.; W. R. E. Hodgkinson, Ph.D.; E. Grant Hooper; H. A. D. Jowett,

D.Sc.; H. R. Le Sueur, D.Sc.; F. E. Matthews, Ph.D.; G. T. Moody, D.Sc.; A. G. Perkin, F.R.S.; W. J. Sell, D.Sc., F.R.S.; John Wade, D.Sc.

Anniversary Dinner.

The Anniversary Dinner was held at the Whitehall Rooms on Friday, March 22nd, at 7 p.m., at which a large number of Fellows and Guests were present.

The following toasts were proposed :—

By the President—"His Most Gracious Majesty the King"; "Her Majesty the Queen Alexandra, their Royal Highnesses the Prince and Princess of Wales, and the other Members of the Royal Family."

By the Right Honourable Lord Rayleigh, O.M., F.R.S., President of the Royal Society—"The Chemical Society," coupled with the name of the President.

By Sir William Ramsay, K.C.B., F.R.S., President-Elect of the Chemical Society—"Scientific Societies," coupled with the names of the Right Honourable Lord Kelvin, O.M., G.C.V.O., F.R.S., and Professor E. Ray Lankester, F.R.S., President of the British Association for the Advancement of Science.

By Prof. Henry E. Armstrong, F.R.S., Past-President of the Chemical Society—"Education," associated with the names of Mr. T. H. Warren, Vice-Chancellor of the University of Oxford; Sir Arthur W. Rucker, F.R.S., Principal of the University of London; and Sir John Wolfe Barry, K.C.B., F.R.S., Chairman of the Executive Committee of the City and Guilds of London Institute.

Prof. T. E. Thorpe, C.B., F.R.S., Past-President of the Chemical Society—"The Guests," coupled with the names of Geh. Rath Professor Dr. Emil Fischer, F.R.S., and Professor J. A. Ewing, F.R.S., Director of Naval Education.

After the President had given the Loyal Toasts, the Right Honourable Lord Rayleigh, O.M., proposed "The Chemical Society."

He said the toast would require but little commendation from him in such a company as was assembled. Although most of his time had been given up to the study of physics, he had always taken the keenest interest in their science, and at an early age had served a sort of apprenticeship to it, having managed to burn his fingers rather seriously with phosphorus before he was thirteen. Their science was so extensive and grew with such rapidity that many of its branches were but little known to him. As examples of this growth, he referred to the development of the aniline dye industry, which had become of immense theoretical and practical importance, and to the various branches so intimately connected with the name of Dr. Emil Fischer. In some aspects, chemistry might be regarded as a branch of physics, and only lately he had been looking over those wonderful papers of Willard Gibbs which were still the foundation of that branch of chemical science, and which had recently been collected and re-published.

Professor Meldola was a man of many and varied attainments. Primarily he was a chemist, but there were few departments of science with which he was not connected, and therefore in giving the toast of the Society he would couple with it the name of its President.

The President said he was deeply indebted to those present for the very kind reception which they had given to the toast proposed by the distinguished President of the Royal Society. He could not help feeling that this was one of those rare occasions that fall to the lot of the official representative of one of the scientific societies to speak to a somewhat wider public than his own immediate circle of colleagues who meet within the walls of the scientific societies, and he would take this opportunity of saying a word or two as to the work of these societies. He feared there was only too much truth in the accusation that this is an unscientific nation. Still, he would have it known that in societies like that assembled and in kindred societies there were banded together small armies of ardent workers who were keeping alight the torch of scientific research, and that, however unscientific nationally, when the time of scientific enlightenment arrived he hoped this would count to our credit and for merit. With regard to the Chemical Society in particular, he felt disposed to join issue with Lord Rayleigh as to whether chemistry should be regarded as a branch of physics or physics as a branch of chemistry. He claimed that in its ultimate association with other departments of science, chemistry was as far-reaching, as cosmopolitan, as any branch of science which was being cultivated at the present time. The Chemical Society was in an exceedingly flourishing condition. It was a venerable Society, founded in 1841, and granted a Charter in 1848. It had therefore arrived at what, according to the Civil Service estimates, would be considered as the year of dotage, instead of which he regarded it as only just entering its prime. During the last few months the Society's ranks had been thinned by the hand of death in the most lamentable way. All its honorary and foreign Russian members, Beilstein, Mendeleeff, and Menschutkin, had been lost, and in France Moissan had passed away, and, quite recently, Berthelot. He was sure those assembled would like it to be known how deeply they sympathised with their foreign *confrères* on the international loss which science had sustained by the death of these distinguished chemists. The Society had a membership of nearly 2900, and was spending from £4000 to £5000 a year in printing and publishing the *Transactions*, *Proceedings*, and *Annual Reports*. Of the value of these publications he need say nothing, for they were sufficiently well known, and if any justification for the Society's existence were ever needed its publications might be pointed out as the one great work which it had so successfully carried on. The editorial department was omnivorous. In the pages of the *Journal*, room was made for atoms and electrons, and even corpuscles. They all received perfectly impartial editorship, and if the new President would forgive the reference, space was even found for organic chemistry! Among the self-imposed duties of the President was the delivery of an Annual Address, and that afternoon he had been dealing with a subject he had closely in mind, namely, the position of chemical research in this country. He had come to the conclusion that there was an immense deal of chemical talent, of chemical faculty, but that there was an enormous wastage going on all over the country owing to unfavourable conditions, some of which he had endeavoured to analyse in the course of his Address. That was a very deplorable state of affairs, for which he saw no immediate prospect of any remedy. He thought gratitude should be expressed for any checks to this wastage that might be in existence, and that it was the duty, not only of the Chemical Society as regards its own science, but the duty of the scientific world as a whole to give recognition to those agencies which were at work, helping to check this wastage of what he and many others considered to be one of the most valuable assets possessed by the country, namely, the original faculty of scientific work. Of such agencies he would mention the 1851 Exhibition Scholarship, the Fellowship given by the Salters' Company, and the Carnegie Scholarships. As to Research funds, the Government made a grant to the Royal Society, but chemistry could only come in for its share along with other sciences. Then there was the Research Fund of the Chemical Society, from which there accrued the modest income of some £220 per annum, and on account of that income being so modest its allotment had to be limited to workers for the purchase of expensive materials and apparatus. The fund had been augmented recently by the munificence of the Goldsmiths' Company, who had added £1000 to it. He would take this public opportunity of expressing the appreciation of the whole scientific world at the munificence of this same Company, which had so splendidly endowed the Lawes Agricultural Institute by a gift of £10,000. Then it was hoped that in a short time the sum of £2700 would be added to the Research Fund of the Chemical Society in the name of a distinguished

Past-President, Sir W. H. Perkin. Much more could be done if there were greater reserves to fall back upon. It had always been a point of ambition to him to see the Research Fund in such a position as would enable the Society to give personal grants to workers, so that they could each secure the services of competent men to co-operate with them in their work. That point appealed particularly to teachers like himself. All teachers had had brilliant young men passing through their classes who had been compelled to go out into the world as soon as possible to earn their living, and thus the country had practically lost the benefit of their capabilities. If by some such endowment as that alluded to teachers were enabled to capture talent of this kind and keep it going, the chemical research of the country would be an enormous gainer in the long run.

Sir William Ramsay, K.C.B., proposed "Scientific Societies." After mentioning many of the learned Societies of Europe and America, he asked why were they banded together. There were important reasons. One was that the young members were enabled to meet the old, which gave great encouragement to the younger men, and their elders found pleasure in knowing them, but the chief reason was that they all had at heart the advancement of knowledge. They desired to increase the sum total of the knowledge of the phenomena of the world. Their desire to know was insatiable, and they were willing to make sacrifices to that end. In that way they founded a brotherhood with all others who were working like themselves, independent of politics and independent of nationality. For these reasons, he asked them to drink the toast.

Lord Kelvin, O.M., G.C.V.O., was the first to respond, He said he found it very difficult to distinguish between the scientific societies for which he had to reply. He believed "Physics" was the subject for which he was specially responsible. But chemistry—how was it distinguished from physics? For fifty-three years he had endeavoured to teach natural philosophy, which was Scotch for physics, and he never could distinguish between physics and chemistry. Well, what was physics and what was chemistry? He would define them together as the science of Force. They heard much at present of the breaking up of atoms, but when they heard of an object from which something had been chipped, it could not have been an atom. He had read in the newspapers of the death-bed of an atom, and yet chemists were going to be told that there was no such thing as an atom! Whether there were many atoms of a different kind was a matter for investigation, but whether each atom of its own kind remained for ever unchanged or not was a subject much discussed. He was not then going to give an opinion upon it, but it was better not to call a thing an atom when it was broken. As to chemistry, he had great sympathy with it. Lord Rayleigh burnt his fingers with phosphorus when he was thirteen. Well, he (Lord Kelvin) had burnt his fingers with phosphorus when he was eighty-two, a thing but few chemists or physicists could say.

Prof. E. Ray Lankester also responded. Scientific societies at the present time were somewhat limited in their objects, or at any rate in their possible activity. He thought they should become something more like the ancient guilds of the great cities of Europe, and endeavour to obtain large funds from those who had benefited and had made fortunes out of the knowledge discovered by the devotees of these sciences, and to employ those funds in development on their own particular lines. He was astonished to learn that the Chemical Society had a Research Fund that produced only £220 a year. When they heard of the large fortunes made by the application of chemistry, he felt that one reason why they did not get more was some want of organisation to enable the societies to secure a very much larger proportion of the wealth gained from the increase of scientific knowledge. In the future he thought they should try to make one large scientific society, something like a guild, or ancient college, or brotherhood, which would hold property for the benefit of a great cause. He ventured to say that would be a much better way to advance science than by gifts of money to mixed corporations, such as universities. He had no faith in universities as promoters of scientific knowledge. Judging from the use made of the funds of the University of Oxford, no one could say that it was desirable to entrust any large sum of money, at the present moment, at any rate, to that University for the promotion of scientific research. The same would apply to the University of London. But societies, such as he suggested, could apply such funds without any danger of their being perverted to secondary uses.

Prof. Henry E. Armstrong proposed the toast of "Education." Speaking of the Universities, he said a head and centre was absolutely necessary for classical activity, but they could not but feel that it was the duty of the Universities to exact from their sons also some understanding of science. Some knowledge of experimental phenomena should be aimed at in all culture.

Mr. T. H. Warren responded first. He said that chemistry at Oxford was not what it ought to be, but its position was far different from that which it occupied some years ago. The universities were reviving the traditions of olden times. At Oxford there was a great school of chemistry, and there were many young chemists there who would be heard of before long.

Sir Arthur W. Rücker next responded. He said it was the duty of a University to teach and to add to knowledge, and he confessed to receiving a shock at what Professor Ray Lankester had said. He stoutly defended the University of London, and added that after all education was growing, and we need not despair of English education.

Sir John Wolfe Barry also responded. He said he looked forward to great results from the Colleges at South Kensington. Speaking as an engineer, he thought his profession might be stated to rest upon chemistry, which taught them the composition and properties of materials. Civil engineers were deeply indebted to the Chemical Society.

Prof. Thomas Edward Thorpe proposed "The Guests." Dr. Emil Fischer and Prof. J. A. Ewing responded.

PHYSICAL SOCIETY.

Ordinary Meeting, April 26th, 1907.

Prof. J. Perry, F.R.S., President, in the Chair.

A paper on "*Electrical Conduction produced by Heating Salts*" was read by Mr. A. E. Garrett.

The experiments described are divided into two series. The first, of a preliminary nature, consisted in testing a large number of inorganic compounds up to a temperature of 360° C. Several compounds, chiefly halogen salts, were found to produce easily detected conductivity when heated. In the case of zinc iodide, conductivity could be detected at the ordinary temperatures of the laboratory. The second series was confined to special cases in order to ascertain the causes of the increased conductivity. It was found that in all the cases tried a formula of the form

$I = a\theta^{\frac{1}{2}} e^{-\frac{b}{\theta}}$; where I = saturation current, a and b constants, and θ the absolute temperature, represents with fair accuracy the connection between the saturation-current and the absolute temperature. Saturation-currents were obtained for both positive and negative ions. Moisture was found to be necessary in some cases in order that conductivity should occur; this was particularly the case with zinc iodide. The negative ions were shown to be true charged centres as they could be deflected by a magnetic field. The conductivity was stopped, when using zinc iodide, by a layer of aluminium foil 0·0008 cm. in thickness. The velocities at different temperatures and pressures were found for the positive ions produced by the iodides of zinc,

lead, bismuth, and cadmium. The positive ions from the zinc, lead, and bismuth salts move with the same velocity under the same conditions, those from cadmium move about twice as quickly. These ions seem to undergo simplification as the temperature is raised. One of these simplifications occurs at 210° C. with pressures 10 to 25 mm. of mercury. These and other considerations point to the fact that the positive ions must be charged centres loaded with considerable amounts of the products due to the chemical changes which the heated salts undergo: in fact, ions similar to those observed in recently prepared gases, phosphorus, &c. The velocities of the negative ions, from iodides of calcium, barium, and zinc, were obtained for temperature 215° C. at different pressures. The negative ions from all these compounds move with the same velocities under similar conditions of temperature and pressure. The rate of decay of zinc iodide at 25 mm. pressure and 260° C. was measured. For the first part of the heating it was found that the results could be represented by the sum of two exponential terms, but that after about one and a half hours no further decay took place.

Dr. R. S. Willows expressed his interest in the paper, and said that experiments similar to the author's had recently been described by J. J. Thomson in the *Cambridge Phil. Soc. Proceedings*. In the author's experiments there was a chance of chemical decomposition, but this had been guarded against by Prof. Thomson. Electrification could also be obtained by crushing salts in a mortar.

Mr. A. Russell asked if cooling salts produced any electrification.

Dr. Willows said the rate of leak increased with temperature, and he should therefore expect it to be very small at low temperatures.

Mr. W. B. Croft exhibited some Solenoids which will move under the action of the earth's magnetic field.

In showing Ampère's experiments it is not very easy to complete the theory of magnetism by making a solenoid point to the north. Many years ago Ritchie made a solenoid with an iron core, which acted as a motor with the help of a mercury commutator. A copper solenoid without core was shown which had been made to rotate in this manner. The method is unsatisfactory and uncertain, owing to the rigidity assumed by the skin on the surface of mercury in certain conditions. The Ampère mercury contacts cause no difficulty when a wire rotates on its own axis, but there are strong hindering forces when the wire is pushed through the mercury, partly from the skin and partly from amalgamation.

The best pattern for a solenoid is suggested by the moving coil of an electro-dynamometer. Two of such were shown, which were conveniently worked by four dry cells in series. Each of these was hung with very thin metal strip by bifilar suspension, the threads about 5 ins. long and one-tenth inch apart. The bifilar control makes the movements manageable: it is convenient to set the coils N. and S., or the axis of the corresponding magnets E. and W., so as to make these swing up to the meridian when a current is sent through the coils. There were also shown some wire models of magnetic lines approximately made to scale so as to represent the horizontal, vertical, and total lines of the earth.

There was also exhibited a thick copper wire of 6·28 cm. radius, which will give a unit magnetic field at the centre when ten ampères is flowing. A long magnet was hung up at the side so as to show the effect of a magnetic pole being attracted to the centre of the coil, running right through and being repelled on the other side.

The Chairman bore testimony to the great rigidity of the surface of mercury after it had been exposed to the air.

Mr. A. Campbell said this difficulty could be partly overcome by covering the surface of the mercury with amalgamating solution.

Dr. Chree believed that solenoids had been used in declinometers in Japan, but there did not appear to be any good reason for such an application.

Mr. W. S. Tucker read a paper on "*The Influence of Pressure upon Convection Currents, and a Criticism of J. Stark's Relation between Cathode Fall of Potential and Temperature.*"

Stark employed as cathode a wire mounted radially in a globe-shaped vessel. The wire was heated electrically and its resistance and hence its temperature determined. His relation for constant temperature was employed, viz.:—

$$K = K_n + \frac{k'}{pf^{\frac{1}{2}}}(i - x'pf)^{\frac{1}{2}};$$

where K and K_n refer to total and normal cathode fall, p the pressure, i the discharge current, f the area of cathode covered with negative glow, and k' and x' are constants. His results with the heated cathode suggest the modification—

$$K = K_n + \frac{k\,T}{pf^{\frac{1}{2}}}\left(i - \frac{xpf}{T}\right)^{\frac{1}{2}};$$

where T is the absolute temperature of the air in the cathode dark space, supposed to be that of the cathode. He refers to the weaknesses of the method: (i) the conduction of heat away from the wire by its leads causes the observed mean temperature to be too low, (ii) the error made in assuming the cathode dark space temperature to be that of the heated cathode. The author's apparatus was devised to show how seriously these weaknesses affect Stark's results. A similar vessel having approximately the same capacity was taken and supplied with a similarly mounted wire for a cathode. Its temperature was measured at the central part of the wire only, fine potentiometer wires being connected at points well removed from the junction with the leads. Within the same vessel a fine platinum wire was mounted parallel to the cathode and about 4 mm. distant. By means of this wire the heating effects of the cathode on the air in its neighbourhood could be measured. The part played by convection currents was determined from a series of curves connecting cathode and thermometer temperatures at different pressures. It was shown that convection losses varied sufficiently both with pressure and temperature to affect the curves from which Stark derived his equation. Observations were also taken when the distance between thermometer and cathode was varied, a low pressure being used so that convection effects were small. A great diminution of temperature with distance was observed, indicating a considerable error in Stark's assumption that the cathode dark space has a temperature approximating to that of the cathode. The heating effect of a sheet cathode was examined, and the observations showed it to be more reliable than a wire. The author's curves show very different convection effects to those obtained by Prof. Bottomley, who employed a cylindrical vacuum tube. The cooling effect increases from pressures of about 15 cm. to those near 10 cm., then decreases first gradually, then rapidly. An approximate value of thermal emissivity for the bright wire was obtained which at 400° C. is near that of Schleirmacher. Reference is made to the observations of temperature in the discharge obtained by Prof. R. W. Wood, and the importance of the convection effects is suggested. Owing to convection Wood's values would probably be too high.

Mr. S. G. Starling expressed his interest in the paper, and said the curves showing the variation in the convection currents were very valuable.

Mr. A. Campbell asked if the thermometer wire employed reached its steady state gradually or whether it overshot the mark and returned gradually to it.

Mr. Duddell pointed out that in some of his experiments he had found that the overshoot effect was due to flow of heat along the thermometer wire. A quick working instrument would approach the steady reading gradually.

Mr. J. A. Tomkins exhibited a Simple Apparatus for Mechanically Illustrating the Tangent and Sine Laws.

Simple apparatus for mechanically testing the tangent and sine laws were described in 1887 in Ayrton's "Practical

Electricity" and again in his more recent work published in 1897. Mr. Tomkins' apparatus, although inferior to some of Prof. Ayrton's, is extremely simple in construction and can be used equally well for illustrating the tangent or the sine law with good results. A weight is suspended by a fine thread from a hook, o. Attached to this thread at N there is a second thread passing over a pully P and terminating in a scale-pan for carrying weights. The pulley is fixed to an arm, capable of rotation about the centre C, which can be clamped in any desired position. Two scales are attached to the apparatus in such positions that the reading of one scale is proportional to the tangent of the angle made by the thread ON with the vertical, while the reading on the other is proportional to the sine of this angle. The thread ON represents the galvanometer needle, the tension in the vertical thread the controlling force, and that in the thread NP the variable deflecting force.

ROYAL INSTITUTION.

Annual Meeting, May 1st, 1907.

The DUKE OF NORTHUMBERLAND, President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1906, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy-Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read.

Thirty-six new Members were elected in 1906, and sixty-three lectures and nineteen Evening Discourses were delivered.

The books and pamphlets presented amounted to about 216 volumes, making with 782 volumes (including periodicals bound) purchased by the Managers, a total of 998 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors for their valuable services to the Institution during the past year.

The Chairman announced that the Managers had awarded the Actonian Prize of One Hundred Guineas to Madame Curie, as the author of the essay "Recherches sur les Substances Radioactives."

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Sir William Crookes.

Managers—The Rt. Hon. Lord Alverstone, The Rt. Hon. Earl Cathcart, Sir Benjamin Baker, W. A. B. Burdett-Coutts, Dr. Donald W. C. Hood, George Matthey, The Rt. Hon. Lord Lister, Francis Elgar, Sir Andrew Noble, Bart., Henry F. Makins, Sir W. H. Perkin, Thomas Edward Thorpe, Sir William H. White, Alexander Siemens, and The Rt. Hon. Sir James Stirling.

Visitors—Arthur N. Butt, Dugald Clerk, William A. Frost, Sir John Craggs, George F. Deacon, Robert K. Gray, Edward Dent, Major E. H. Hills, Charles E. Groves, Sir John Jackson, Frederick G. Henriques, Edward Kraftmeier, Francis Lys Smith, James Swinburne, and Alfred F. Yarrow.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th instant, Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. J. H. Morrell, Dr. O. Oberländer, and Mr. F. L. Pattisson were elected Members. It was announced that His Grace the President had nominated the following Vice-Presidents for the ensuing year: — The Right Hon. Lord Alverstone, G.C.M.G., Sir Benjamin Baker, K.C.B., Dr. Ronald W. C. Hood, C.V.O., Sir Andrew Noble, K.C.B., Alexander Siemens, Esq., The Right Hon. Sir James Stirling, Sir James Crichton-Browne (Treasurer), and Sir William Crookes (Honorary Secretary).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 15, April 15, 1907.

Application to Pyridine of the Method of Direct Hydrogenation by Nickel.—Paul Sabatier and A. Mailhe. Considering pyridine, C_5H_5N, as a benzene in which one nitrogen atom of the molecule has been replaced by the group CH, the authors have applied to it the method of direct hydrogenation in contact with divided nickel, which applies readily enough to the aromatic group. The expected transformation into piperidine, $C_5H_{10}NH$, did not, however, occur. The greater part of the pyridine vapours passed unchanged over the nickel, but a slight diminution in volume was observed, most marked between 160° and 180°. The condensed liquid exhibited characteristics indicating the presence of a primary or secondary amine, and fractional distillation furnished a small quantity of this, boiling at 104°. This is also the boiling-point of piperidine, but the liquid did not correspond to the requirements for piperidine, and was proved to result from a rupture of the nucleus, giving amylamine, $CH_3.CH_2.CH_2.CH_2.CH_2.NH_2$. On heating pyridine more strongly, towards 350°, the destruction is more rapid, quantities of ammonia and of pentane being evolved. The vapours of piperidine passed over reduced nickel at 250° were found to be converted entirely into hydrogen and pyridine.

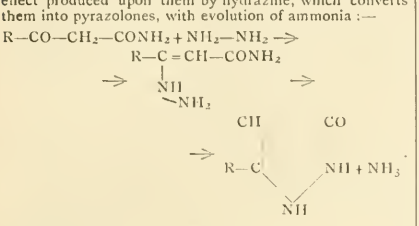
Reduction of Magnesia by Carbon.—Paul Lebeau.—Magnesium oxide is the only one of the metallic oxides not hitherto clearly shown as capable of being reduced by carbon. The author has demonstrated this reduction in the electric furnace, obtaining as the result magnesium and magnesium carbide. These products are largely destroyed by the furnace gases, which contain quantities of CO, a gas readily attacked by magnesium. The temperature at which the reduction takes place must be near the boiling-point of magnesium oxide.

Aluminium Sulphide and its Combinations with Magnesium Sulphide and with Iron Sulphide.—Marcel Houdard.—The sulphides of magnesium and aluminium are so stable that they have been found incapable of reduction in the electric furnace. This author, by heating mixtures of the two sulphides with carbon in a stream of sulphuretted hydrogen, has been able to obtain a double compound of crystalline structure, corresponding to the formula Al_2S_2Mn. Similarly, with a mixture of the sulphides of aluminium and iron, a double compound, Al_2S_4Fe, was obtained. These bodies are comparable to the aluminates.

A New Chloride of Tantalum.—C. Chabrié.—Hitherto the only known chloride of tantalum is $TaCl_5$; the new chloride corresponds to the oxide Ta_2O_2. It is prepared by reducing the pentachloride with sodium amalgam. Analysis gave the following results:—Numbers obtained—Ta, 63·83; Cl, 23·85; H_2O, 12·22; total, 99·90. Numbers calculated for formula $TaCl_2.2H_2O$—Ta, 63·1; Cl, 24·4; H_2O, 12·5; total, 100·0. *Properties.*—$TaCl_2$ is a green crystalline powder soluble in water to some extent. It turns brown in air. Heated in air, it decomposes, losing chlorine and being converted into tantalic anhydride.

Method of Synthesis of the Non-substituted β-Ketonic Amides.—Ch. Moureu and I. Lazennec.—The β-ketonic amides, $R—CO—CH_2—NH_2CO$, are produced from the acetylene amides by warming their alcoholic solutions with a secondary amine, preferably piperidine. In this the yield is proportional to the amount of piperidine used, for, in performing its part of catalyser, it forms an intermediate product with the acetylene amide, which then, by hydrolysis, is converted into the corre-

sponding β-ketonic amide with regeneration of the piperidine. Several of the β-ketonic amides thus produced are described. Their constitution is established from the effect produced upon them by hydrazine, which converts them into pyrazolones, with evolution of ammonia :—



Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 6, 1907.

Atomic Weight of Indium.—Frank Curry Mathers.—Thiel found In = 115·4 from the ratios In : $InCl_3$ and In : InI_3, but very probably this value is too high, because loss is caused owing to volatilisation when the haloids are dried; also the trichloride and triiodide may contain basic salts, and it is difficult to free indium metal from moisture and foreign salts. The mean of four results obtained in experiments in which the ratio of $InCl_3$: AgCl was determined gave 115·05, while three experiments with the corresponding bromine compounds gave 114·81. No correction was made for the solubility of silver chloride. Brauner, applying a correction for solubility, found 114·9 from the ratio $InCl_3$: AgCl. The author for the purpose of determining the atomic weight of indium purified commercial indium metal by dissolving in hydrochloric acid, precipitating off insoluble sulphides with sulphuretted hydrogen, and then precipitating the filtrate with ammonia and ammonium chloride. The hydroxides of iron, indium, and aluminium and small quantities of zinc hydroxide were thus obtained. The precipitate was washed, dissolved in hydrochloric acid, and ammonia and ammonium chloride again added; this process was repeated four times, to remove the zinc as completely as possible. Then most of the iron was removed by adding potassium rhodanide and shaking with ether, and the solution was finally electrolysed, after the free acid had been boiled off. Indium metal was thus obtained in the form of crystals. It was dried at 120°, fused in a current of hydrogen, and then used to prepare the different derivatives. Firstly, indium was converted into the sulphate by adding sulphuric acid to it in a platinum dish, and heating to 400°. However, indium sulphate is very hygroscopic, and retains traces of sulphuric acid, while if heated strongly it decomposes, and hence no accurate results were obtained. Secondly, the ratio $InCl_2$: AgCl was determined by allowing gaseous hydrochloric acid to act on the metal. As long as metallic indium was present the dark brown monochloride, InCl, was formed, but as the action of the acid continued the light yellow $InCl_2$ was produced. This was then redistilled in a current of carbon dioxide. The dichloride was dissolved in nitric acid and precipitated with silver nitrate, but very discordant results were obtained. Thirdly, the ratio $InCl_3$: AgCl was found by heating pure metallic indium in a current of chlorine. The trichloride dissolved to a clear solution in water only when some dilute nitric acid was added, probably because not all the dichloride had been converted into trichloride, and thus some metallic indium separated, $3InCl_2(+H_2O) = 2InCl_3 + In$, or possibly indium trichloride dissociates to some extent into the dichloride and chlorine. In later experiments the sublimations were carried out in a current of carbon dioxide to which some chlorine had been added. The mean of six experiments in which the atomic weight of silver was assumed to be 107·93, and that of chlorine 35·473, gave In = 114·88. The ratio $InBr_3$: AgBr was determined similarly, and as a result it was found that In = 114·86 if Br 79·953. Thus probably In = 114·9 is correct.

Ferromagnetic Compounds of Manganese with Boron, Antimony, and Phosphorus.—E. Wedekind.—The author has already shown that manganese boride is ferromagnetic, and the antimonide, MnSb, possesses the same property. Thus possibly definite chemical compounds of manganese with other elements are the carriers of the ferromagnetism, and the same components may yield magnetic and non-magnetic compounds which differ chemically in stochiometric composition. This hypothesis is supported by the fact that some compounds, for example, manganese phosphide, have been described by different investigators as magnetic and also as non-magnetic. When antimony acts on liquid manganese, only one stable compound, MnSb, can be isolated. This is more magnetic than manganese boride, MnB. Both borides, MnB and MnB_2, are ferromagnetic, but it is very difficult to separate MnB completely from MnB_2, and probably MnB_2 is non-magnetic, while the carrier of the magnetism is the compound MnB. The crystalline phosphide, Mn_5P_2, is distinctly magnetic, as is also Mn_3P_2. No phosphide, MnP, could be prepared. The investigation of the question of the degree of permeability of the ferromagnetic compounds of manganese compared with those of iron presents great difficulties, but the author found that powdered manganese boride, MnB, is more than half as strongly magnetic as powdered iron, whereas compact MnB is about a quarter as strongly magnetic as soft iron. The compact antimonide is nearly twice as strongly magnetic as MnB.

Thio-acetic Acid.—J. Houben and H. Pohl.—To prepare thio-acetic acid, $CH_3.CS.SH$, carbon disulphide is added slowly to a cooled solution of methyl magnesium iodide, which gradually turns a dark red-brown, and begins to emit a very piercing and characteristic smell. The liquid often separates into two layers. It is cooled, and first ice is added and then cooled hydrochloric acid. The red-brown ethereal layer is removed, extracted with dilute soda solution, and the solution is then extracted five or six times with ether to remove impurities of the nature of mercaptans. Ice-cold hydrochloric acid is added, and the free thio-acid taken up in ether. The acid is a reddish yellow strongly smelling oil, its odour recalling mercaptan, allyl sulphide, and acetic acid. It is practically insoluble in water. Its analysis leaves no doubt that its composition is represented by the formula $CH_3.CS.SH$, and its low boiling-point (37° under 15 mm. pressure), and other properties show that it is not a polymer of $C_2H_4S_2$. The specific gravity at 20° is 1·24. It yields neutral soluble salts with alkalis. It is a very strong acid, and replaces acetic acid in its salts. It does not ignite easily, but on warming it burns with a blue flame, yielding sulphur dioxide and carbon.

Thiosulphates.—Julius Meyer and H. Eggeling.—Two isomeric potassium sodium thiosulphates can be obtained, in one of which the sodium, and in the other the potassium, is directly bound to the sulphur. Thus the formulæ are $KS.SO_2.ONa$ and $NaS.SO_2.OK$. Exactly the same isomerism is exhibited by some double salts with heavy metals, the heavy metal being bound with the sulphur in one case and with the oxygen in the other. The silver alkali thiosulphates containing ammonia can yield yellow salts with the stronger alkalis; these are analogous to the yellow copper salts in which the copper is undoubtedly monovalent. Thus the allied elements, silver and copper, form yellow alkali double thiosulphates, as well as white salts, which are possibly isomeric, the formulæ being $AgS.SO_2.O$ and $CuS.SO_2.O$, or $AgO.SO_2S$ and $CuO.SO_2.S$. Most double thiosulphates are not stable, and only the silver and lead salts of the stronger alkalis can be kept without undergoing decomposition. Moreover, the heavy metal salts decompose if an attempt is made to re-crystallise them from water, and hence some metals can be pre-

cipitated from their hot solutions by thiosulphate solution instead of sulphuretted hydrogen.

Bismuth Iodide. — Lothar Birckenbach. — Already noticed.

Hydrolytic Decomposition of Sodium Chloride.—Fr. Emich.—A small quantity of sodium chloride is introduced into a platinum crucible raised to a yellow heat (temperature about 1100°), and then about 1 cc. of water, which is naturally at once converted into the spheroidal state. When after about half a minute half of the water has evaporated, the drops are allowed to fall into about 100 cc. of dilute blue litmus. Before the crucible has quite cooled the small quantity of fused salt which adheres to it is taken up with water, and the solution is added to dilute red litmus. The changes of colour of the litmus solutions show that the water has become acid and the salt alkaline.

MEETINGS FOR THE WEEK.

TUESDAY, 14th.—Royal Institution 3. "Alfred Stevens, the English Sculptor and Painter," by D. S. MacColl.

WEDNESDAY, 15th.—Society of Arts, 8. "Trypanosomiasis, or Sleeping Sickness," by Herbert W. G. Macleod, M.D.

—— Microscopical, 8. "Diffraction Rings due to a Circular Aperture," by A. W. Porter and P. F. Everitt. "An Improved Vertical Illuminator," by E. M. Nelson. Exhibition of Pond Life.

THURSDAY, 16th.—Royal Institution, 3. "Spectroscopic Phenomena in Stars," by H. F. Newall, F.R.S., &c.

—— Chemical, 8.30. "Relation between the Crystalline Form and the Chemical Constitution of Simple Inorganic Substances, by W. Barlow and W. J. Pope. "Experimental Investigations into the Process of Dyeing," by J. Hubner. "Some Derivatives of *p*-Pyranol allied to certain Derivatives of Brazilein and Hæmatein," by W. H. Perkin, jun., and R. Robinson. "Mixed Semi-ortho-oxalic Compounds," by G. D. Lander. "The Mechanism of Bromination of Acylamino-Compounds," by J. B. Cohen.

FRIDAY, 17th.—Royal Institution, 9. "Seiches in the Lakes of Scotland," by Prof. George Chrystal, M.A., &c., assisted by E. M. Wedderburn.

SATURDAY, 18th.—Royal Institution, 3. "The Limits of the Dramatic Art," by Arthur Bourchier, M.A.

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NOTE ON THE DETERMINATION OF VOLATILE FATTY ACIDS IN BUTTERS (REICHERT NUMBER).

By L. de KONINGH.

The following modification of the Reichert process may perhaps be found useful when the quantity of butter at disposal is very small and when an early analysis is required.

The butter is melted in a test-tube placed in hot water, and 2·5 grms. of the clear fat are saponified with 12·5 cc. of normal alcoholic caustic potash in a flask fitted with a long vertical tube. When saponified, 25 cc. of distilled water are added, and the whole evaporated in a basin to pasty consistency. The soap is dissolved in warm water, made up to exactly 60 cc., and placed in the distilling flask. 15 cc. of normal sulphuric acid are then added, also some fragments of clay pipe. The whole is then submitted to distillation and 50 cc. are collected. The distillate is filtered into a 300 cc. flat-bottomed Jena flask and titrated with N 10 sodium hydroxide, with phenolphthalein as indicator. The result may, however, be too high, as during the evaporation of the soap a not inconsiderable quantity of carbon dioxide may have been absorbed, and the N/10 soda used in the titration, unless freshly made, may have become somewhat carbonated. Therefore 0·5 cc. of N 10 hydrochloric acid is added and the carbon dioxide expelled by rapidly heating the liquid to boiling and then boiling gently for three minutes. The flask is now rapidly cooled and the titration continued ; the liquid should, of course, be colourless. From the total number of cc. of N/10 soda used 0·5 cc. is then deducted.

The following experiment shows that, with care, there is practically no loss of acid :—50 cc. of water, free from carbon dioxide, were mixed with a few drops of butyric acid and neutralised with lime-water equal to 11·5 cc. of N 10 soda ; 0·5 cc. of N 10 hydrochloric acid was then added, and the liquid boiled for three minutes. One-eleventh part of the solution had evaporated. Additional lime-water, to the extent of 0·4 N 10 soda, was now required ; total, 11·9 cc. of soda, which, minus 0·5 cc. of acid added, equals 11·4 cc. The loss in acid during the boiling consequently amounted to 0·1 cc. soda.

A NEW INTERMEDIATE PRODUCT FROM THORIUM.

By OTTO HAHN.

Many articles on the properties of radio-thorium, and more especially on its relation to thorium, have recently appeared. In my first complete communication on radio-thorium (*Jahrbuch d. Radioactiv. u. Elektron*, iii., 330) I alluded to the possibility that it is a decay product of thorium, that thorium itself emits no rays, and the activity of ordinary thorium is due only to radio-thorium and its decay products. In order to signify this I chose the name radio-thorium for the strongly active product.

The articles of G. A. Blanc (*Chem. Centralblatt*, 1906, ii., 1107) and of Elster and Geitel (*Phys. Zeit.*, 1906, 445) confirmed and extended our knowledge of the radio-active properties of radio-thorium and their agreement with those of thorium, so that there can be no doubt about the identity of the two substances which emit the emanation.

Elster and Geitel succeeded in obtaining from ordinary thorium a small quantity of an oxide which was always about twelve times as strongly active as ordinary thorium oxide. They have thus effected a certain concentration of radio-thorium. Also G. A. Blanc, by the action of barium sulphate, obtained from 6 kg. of thorium nitrate a few milligrammes of a product, which was some thousand times as strong as thorium oxide and also retained its activity.

The relation of the activity of thorium minerals to the amount of thorium they contain was discussed in the articles of Boltwood (*Amer. Journ. of Science*, xxi., 409) and Dadourian (*Phys. Zeit.*, 1906, 453), who obtained exactly the same result quite independently. Both workers found that the activity of thorium minerals referred to the same amount of thorium is a constant number ; a result which shows that radio-thorium is a decay product of thorium.

Thus the relations are the same as in the case of uranium and radium, in which, from the constancy of the proportion of uranium to radium in the most different minerals, conclusions can be drawn about their genetic relationship.

The researches of Boltwood and of Dadourian were not limited to thorium minerals ; commercial thorium preparations were also investigated. It was then found that commercial thorium nitrate has less than half the activity which it should show according to the amount of thorium it contains—a very remarkable result. The two investigators used quite different methods of measurement. Boltwood compared the activity by means of the effect of the α-rays, by the method first described by McCoy (*Journ. Amer. Chem. Soc.*, xxvii., 291 ; *Amer. Journ. of Science*, xxi., 433). Dadourian used his preparations in solution, collected the active deposit resulting from the emanation on a negatively charged wire, and measured the activity thus obtained, keeping the external conditions the same. Recently, Eve (*Am. Journ. Sci.*, Dec., 1906) obtained the same results, comparing thorium minerals and commercial thorium preparations of known composition by means of the γ-rays.

Thus commercial thorium nitrate was always scarcely half as strongly active as it should be.

From these results Boltwood concluded that when thorium nitrate is prepared technically, by some means more than half the radio-thorium is separated from the thorium.

Such a possibility could not be proved directly ; but so extensive a separation would be very noteworthy when we reflect that hitherto all attempts to separate radio-thorium from thorium had either been completely unsuccessful, or, as in Elster and Geitel's experiments as well as those of G. A. Blanc, had been successful only to such an extent that there was hardly any difference in the strength of the activity from that of thorium itself.

I therefore began a systematic investigation of the

activity of commercial thorium preparations of different degrees of purity, in order to find out whether during the purification process any decrease of activity could be detected. These experiments were rendered possible for me owing to the kindness of the firm of Dr. O. Knöfler and Co., of Plötzensee, near Berlin, who placed at my disposal specimens of very different degrees of purity, for which I beg to offer them my hearty thanks.

The activity of the preparations was measured by McCoy's method (*loc. cit.*), which allows the specimens to be prepared in layers which can be made as thin as is desired and are perfectly uniform, so that under the same conditions different preparations can be directly compared with one another by means of their α-activity. Generally, the thorium preparation in question was converted into oxide, and then strongly ignited for a short time in order to convert it into the non-emanating condition. Then it was stirred with chloroform, smeared on an aluminium plate by means of a fine hair-brush, and measured with an electroscope. The aluminium plates had the same form and surface, and the quantity of substance taken amounted generally to 10 to 12 mgrms. Preliminary experiments showed that the results obtained with the same preparations under these circumstances agreed satisfactorily.

Some preparations which were measured already contained a large amount of thorium, but they were always subjected to repeated purification processes. Taking into account the somewhat varying composition of the oxides, the general result obtained was that during the purification process no gradual nor sudden decrease of the activity could be detected with certainty. Variations of the activity, it is true, were obtained, but in opposite directions, while the impure specimens were sometimes found to be weaker than the pure, calculated to the same amount of thorium. This was probably due to small quantities of alkalis, owing to which the layer became somewhat hygroscopic, and caused a rather greater absorption of the α-particles. (It must be remarked that insufficiently strongly ignited ThO_2 is also hygroscopic).

Thus the separation of radio-thorium, if it occurs at all, must have been effected when the raw thorium was prepared from monazite. I therefore investigated some preparations and liquors from the first processes of the working up of monazite, as far as I could obtain them. But the result was the same in this case also. The activity corresponded satisfactorily to the approximate amount of thorium present, and also the undissolved and insoluble residue remaining behind in the working up process showed no appreciable thorium activity after an excess of thorium-X had decayed.

All the specimens examined were fresh products, and came to me directly from the technical process. It is therefore clear that attention must be directed to the variations of activity caused by thorium-X. The measurements were therefore either taken a month after delivery, or they were repeated until equilibrium with thorium-X had ensued.

The above mentioned attempts to find in the preparation and purification of commercial thorium a point at which the separation of radio-thorium takes place, or to show a gradual decrease of activity as the purification process proceeded, have thus led to no result, and the question of the whereabouts of the missing radio-thorium remained open.

I was thus confirmed in the opinion I had previously formed, that the decay of thorium into radio-thorium does not take place directly, but that an intermediate product may exist from which radio-thorium is formed.

Various facts seem to me to point to the existence of such a substance.

According to a private communication from Boltwood, the feebly active thorium nitrate in the course of nearly two years showed no appreciable alteration of its activity. Thus a relatively long duration of life must be deduced for radio-thorium. On the other hand, I had already stated in an earlier communication that the radio-thorium preparations examined by me showed a decided decrease in their activity. In my last communication on the subject I stated that an exact series of measurements was in hand, which would give information concerning the period of decay of radio-thorium, all errors being avoided as far as possible. In order to exclude external influences, such as moisture, &c., the preparation was kept on a little glass dish, the air being excluded by means of a thin plate of mica. Unfortunately, this preparation was smashed on the journey from America, so that again new experiments had to be begun. A preparation was examined for its β-activity in fused glass tubes. Another, analogous to the above preparation, was kept on a watch-glass, which was closed air-tight with a thin mica plate. To avoid electrostatic disturbances the vessels were completely wrapped in tin-foil. The result was that again the activity of the preparations decreased. However, I cannot yet state a definite decay constant, as the decay seems to proceed far more slowly after a time than at first. The order of magnitude of the outside limit of the decay period of radio-thorium seems to be about two years, or perhaps it is still less. I shall shortly return below to the possible explanation why no single numbers could be found for the decay.

Thus the radio-thorium preparations decrease, but Boltwood's weakened thorium does not increase, or not in the same proportion as would be expected if radio-thorium was the direct derivative of thorium. A way out of the difficulty is to be found in the assumption of the existence of an intermediate product between thorium and radio-thorium, with a longer duration of life than that of radio-thorium. This would explain why the feeble thorium preparation mentioned above did not increase in proportion as the radio-thorium preparations investigated by me decreased. It need only be assumed that the thorium preparation is deficient not only in radio-thorium, but also in the intermediate product, the fresh formation of which causes the fresh formation of radio-thorium.

Also the presence of considerable thorium activity in the sediments examined by G. A. Blanc, and Elster and Geitel, can easily be explained if we assume a slower product than one the decay constant of which is less than two years.

In order to prove the possible existence of such an intermediate substance between thorium and radio-thorium, the best way was to compare with one another thorium preparations of the same strength and made in the same way, but of different age, to test whether they showed any difference in activity. The firm of O. Knöfler and Co. kindly placed at my disposal average specimens of pure thorium nitrate of different years, and also some specimens the dates of the preparation of which were accurately known.

In the investigation considerable differences of activity were found, and there was a gradual decrease of activity from the newest to the older specimens. The freshly prepared thorium nitrate showed an activity of the same order of magnitude as that of a corresponding quantity of thorianite, if the activity caused by the uranium and radium in this mineral is deducted. This result agrees with Boltwood's; he prepared thorium nitrate, and proved that its strength was of the right order of magnitude.

For some years the activity then decreases, and seems after about three years to reach a value which remains nearly constant for a fairly long time. Naturally, I had not at my disposal an unlimited choice of well defined preparations; most of the older products were the year's average specimens, which naturally gave no exact numbers. I cannot therefore give a simple curve of the activities found over a large period of time; moreover, it is not certain whether in each case exactly the same conditions were maintained in the preparation.

It is probable that the gradual decrease of the activity of freshly made thorium preparations is caused by the decay of an excess of radio-thorium due to some cause or other, and as a matter of fact the order of magnitude of the decrease is a period of about two years.

After the lowest value of the activity is reached, and has lasted for some time, a gradual increase seems to occur. Thus, some still older preparations, one of the year 1898 and an old specimen of February, 1895, seemed again to show a stronger activity, and the 1895 preparation showed a somewhat higher value than the one three years younger.

In this article I am not giving any figures, as I hope soon to be able to report comprehensively upon a greater selection of thorium preparations of different age. I am now merely indicating the values found.

In the technical preparation of thorium nitrate an intermediate product is separated which emits no α particles. Radio-thorium itself remains with the thorium. Hence, the activity of the nitrate is of the expected order of magnitude immediately after its preparation. The period of decay, and thus the period of the formation of the intermediate product, is longer than that of radio-thorium. The activity of the fresh preparation thus decreases, because the producer of radio-thorium is lacking, and, in fact, decreases with the period of radio-thorium. If the intermediate product was completely separated, and if this had a very long duration of life, the decrease would proceed nearly to zero. But as a matter of fact the duration of life of the intermediate substance is not very great. A first approximation to its decay period seems to be about seven years. Then the intermediate substance is again gradually formed, and with it the radio-thorium. After two years a lowest value of the activity is reached, and then a gradual change occurs. The recovery of the thorium then proceeds with the slower period of the intermediate substance; when this is completely reproduced the activity is again as strong as immediately after preparation, and then remains constant. About forty years would be necessary to reach this value.

Thus from the gradual decrease of the activity of the thorium preparations the existence of an intermediate substance can be shown indirectly.

A positive proof cannot be brought forward till from older thorium preparations, or from any products of the preparation of thorium, substances free from thorium have been obtained which at first show very small activity or none at all, and which then gradually exhibit the specific thorium activity. The characteristic emanation of thorium is a safe test for this, and excludes any possibility of error.

I have arranged a great many experiments to study this point, and I have succeeded in proving directly the fresh formation of radio-thorium. I have three preparations which do not contain an appreciable amount of thorium, and which for over two months have shown a constant increase of their activity. Another small specimen was prepared in November last year, and its increase of activity shows no abatement. Only the effect of the α-particles of the latter was investigated, but some of the newer preparations were in the form of a solution, and from the solutions the increase of emanating power up to a constant amount could be proved.

As in a radio-thorium preparation, even if it was at first quite free from thorium-X, after a month no more change of power of emitting an emanation occurred; if it was examined under identical conditions, the constant increase is a direct proof of the existence of a parent of radio-thorium which differs from thorium.

The experimental results obtained by the above named investigators can be explained without any straining by the existence of this intermediate substance. Clearly they were using preparations which were already some years old, and in which the original excess of radio-thorium had quite, or nearly quite, decayed. Boltwood in his article mentioned above states values for the activity of different commercial thorium preparations which, in contrast to the remarkable constancy of the activity of the minerals, show considerable differences from one another, differences which certainly lie without the limits of error. This could be explained by a difference in the age of the preparations obtained from different sources.

The fact that Boltwood has a weak thorium preparation which for nearly two years has shown hardly any change in its activity seems to me to show that here he has a specimen which lies just at the minimum of its activity; but assuming one intermediate product, as stated above, it should be possible now to detect a slow increase.

Also the periods of decay of the radio-thorium preparations examined by me, which did not quite agree, and which were apparently gradually becoming slower, could be explained by assuming the presence of varying amounts of intermediate substance. It would then, of course, be supposed that the radio-thorium prepared by me from thorianite was not actually pure radio-thorium, but contained a considerable quantity of the intermediate substance.

I refrain from definitely choosing a name for the new substance till its nature has been more closely investigated. When this has been done the name "mesothorium" would seem to me to be appropriate.—*Berichte*, vol. xl., 1462.

PROCEEDINGS OF SOCIETIES

THE ROYAL SOCIETY.

Conversazione at Burlington House.

A well attended Conversazione was held at the Royal Society's Rooms, Burlington House, on May 8th. The following are some of the most interesting exhibits:—

Dr. F. D. Chattaway, F.R.S., showed Copper Mirrors deposited upon Glass from Aqueous Solution.—Although silver is so readily deposited upon glass from aqueous solution as a coherent metallic film that mirrors are extensively manufactured in this way, it has not hitherto been found possible thus to deposit the metal copper, which in so many other respects closely resembles silver. In the mirrors exhibited, the copper has been deposited upon the glass by reducing cupric oxide by an aqueous solution of phenyl hydrazine in presence of potassium hydroxide, which accelerates the action to a remarkable extent. The mirrors are equal in brilliancy and uniformity of surface to silver mirrors, and on account of the colour of the copper are much more beautiful.

Sir James Dewar, F.R.S. The Crookes Radiometer; Motion arrested in very high Vacua, &c.

1. Experiments showing the cessation of radiometer action in very high vacua, made by charcoal cooled in liquid hydrogen or liquid air, even when the instrument is subjected to the concentrated radiation of an electric lamp.

2. Radiometer filled with helium at atmospheric pressure, which is inactive to a charcoal liquid-air vacuum, but becomes active in a charcoal liquid-hydrogen vacuum.

Mr. W. Duddell, F.R.S., showed some Persistent Electric Oscillations.—The oscillations are produced by the method of the "musical arc." In this method a direct-current arc is shunted with a circuit consisting of a condenser and a self-induction in series. The frequency of the oscillations can be varied by altering either the capacity or the self-induction in the shunt circuit. The oscillograph records exhibited show the variations in the potential difference and current when the oscillations are produced. To obtain powerful oscillations at very high frequencies the arc may be placed in hydrogen gas as employed by Paulsen. In the apparatus shown the arc burns in coal-gas, and *no magnetic field* is used to blow out the arc. Experiments in magnetic induction, tuning, and discharge in vacuo are easily demonstrated with persistent high frequency oscillations. The persistent oscillations are of special use for energising the transmitter in wireless telegraphy, as they permit better syntony or tuning to be obtained.

The DIRECTOR OF THE IMPERIAL INSTITUTE exhibited :—

1. Igneous and Metamorphic Rocks of Northern Nigeria. —Typical specimens collected during the course of the Mineral Survey of Northern Nigeria now in progress in connection with the Imperial Institute. Gneisses and schists are widely distributed and represent the oldest rocks of the country. They constitute the main part of the Bauchi Highlands, where extensive and valuable deposits of tin ore (cassiterite) have been discovered. They also cut through the sediments of the surrounding plains. Intrusions of granite are not uncommon and are seen in the chief peaks of the Bauchi Hills. At Igbo a series of metamorphic limestones occurs intercalated with mica schists. A series of twenty specimens is shown. These have been collected by Dr. Falconer, the Principal Surveyor.

2. Tinstone from Bauchi, Northern Nigeria, and Tin smelted from it.—The deposits of cassiterite are already being worked, and the tin smelted *in situ*.

3. New or exceptional Minerals from Ceylon.—These were found during the course of the Mineral Survey of Ceylon now in progress in connection with the Imperial Institute, where the composition of these materials is being investigated.

(*a*) *Zirkelite*.—A rare mineral containing the oxides of titanium and zirconium, together with variable proportions of other oxides. Three varieties are shown: (1) containing 20 per cent of thoria and 1 per cent of uranium oxide ; (2) containing 8 per cent of thoria and from 2 to 5 per cent of uranium oxide ; (3) containing traces of thoria and 15 per cent of uranium oxide. The crystals, which belong to the hexagonal system, differ also in specific gravity. An account of these varieties of zirkelite will shortly be communicated to the Royal Society. In exhibiting variation in the proportions of thorium and uranium the zirkelite of Ceylon shows the same peculiarities as thorianite.

(*b*) *Baddeleyite*.—Notable as a definitely crystalline form of this mineral. Some crystals exhibit twinning, others are untwinned. The mineral is essentially oxide of zirconium.

(*c*) *Thorite*.—Notable as an anhydrous form of the mineral with the high specific gravity of 6. Essentially a silicate of thoria, containing 74 per cent of thoria.

(*d*) *Monazite*.—Consists mainly of phosphates of the cerium metals, notable in containing variable and unusually high percentages of thoria. The three specimens shown contain 10, 15, and 28 per cent of thoria respectively.

4. New Vegetable Products of hitherto unknown composition.

(*a*) Wax of the Raphia palm of Madagascar (*Raphia ruffia*), obtained from the leaves.—This consists principally of two solid aliphatic alcohols, the chemical constitution of which is at present under investigation at the Imperial Institute.

(*b*) Oil of *Origanum hirtum*, or *onites* of Cyprus.—This is found to contain cymene and carvacrol, together with a new terpene and alcohol. It has been introduced into perfumery. The oil of another thyme, *Origanum maru*, of Cyprus, closely resembles oil of marjoram. It contains terpinene, terpinenol, and a new crystalline alcohol, $C_{10}H_{17}(OH)_3$, which is at present under investigation.

(*c*) Oil obtained from the *Pimenta acris* of Mauritius. —This oil contains phellandrene and eugenol, and may be of value in perfumery.

Mr. W. A. DOUGLAS RUDGE showed the Action of Radium and other Salts on Gelatin Culture Medium.—Radium, barium, strontium, and lead salts, when placed in contact with gelatin culture medium, give rise to a kind of cellular growth, which is due to the formation of an insoluble precipitate with the sulphuric acid usually present. Radium salt added to medium from which the sulphuric acid has been removed, causes no growth, but the addition of a soluble sulphate produces a growth at once. Analysis of the growths obtained with radium salts show that they are composed of barium sulphate.

Mr. ULRICH BEHN exhibited a short Glycerine Barometer.—This consists of an air thermometer of the old Italian type, the bulb of which is kept at zero by means of ice in a Dewar vessel. After some weeks the apparatus must be provided with a fresh supply of ice.

Dr. J. R. MILNE showed a Special Camera for the purpose of Automatically Recording the Readings of the Scale of any Instrument.—The purpose of this invention is to enable one, when using any piece of physical apparatus, which has a scale and vernier, to record whenever wished the readings of the latter. The observer effects this by simply pressing a bulb, which causes the camera to make a photograph of the scale and vernier on a small portion of its sensitive plate. The plate is then automatically moved on a step so as to present a fresh surface for the succeeding photograph. The 5 × 4 plates employed can each receive seventy records.

Messrs. PILKINGTON and GIBBS, Ltd., exhibited a Helio-Chronometer.—The helio-chronometer gives Greenwich mean time by a simple direct solar observation. It comprises devices for adjustment in latitude, longitude, level, and azimuth. It is self-correcting for the equation of time by means of a disc divided and engraved to show the month and day ; the disc can be turned to indicate the current date. The underside of the disc is a cam formed to represent the equation of time plotted as a polar curve ; and touching the cam is a lever carrying the upper pierced screen through which the sun can throw a spot of light on to the centre line of the lower screen, the dial being turned about the polar axis to permit this. The imaginary mean sun is therefore advanced or retarded from the apparent sun by the amount requisite to cause the instrument to indicate Greenwich mean time correct to a few seconds.

Hon. C. A. PARSONS, F.R.S., showed some Photographs of Microscopic Diamonds obtained from pure iron heated in a carbon crucible in an electric furnace and rapidly cooled. Scale, 150 diameters.

THE CAMBRIDGE SCIENTIFIC INSTRUMENT COMPANY exhibited :—

1. Prof. Féry's self-contained Radiation Pyrometer.—The pyrometer utilises the heating effect of the "total radiation" from a hot body, focussed as an image of that body by means of a concave mirror. It differs from the already known Féry radiation pyrometer in being entirely self-contained, the image falling upon a minute bi-metallic flat spiral (Breguet spiral). This becomes partially uncoiled as its temperature rises, and a light pointer attached moves over a dial divided to give direct (Centigrade) temperature readings. There are two temperature scales, the higher being appropriate when a sector diaphragm is fixed in front of the pyrometer so as to reduce the effective aperture. Convenient means are provided for sighting and focussing the pyrometer. The instrument is shown sighted on Prof. Féry's electric furnace, with protected carbon resistance.

2. Universal Portable Electrometer, designed by Mr. C. T. R. Wilson, F.R.S.—Gold leaf instrument with very small capacity and fused quartz insulation, suitable for work on atmospheric electricity, radio-activity, &c., and self-contained, with means for standardising the readings, which are very steady even in a fairly high wind.

Dr. ROBERT KNOX and Mr. G. PEARCE showed Skiagraphy of the Human Subject ; examples illustrating the advantages of Reduction in Exposure.

Advantages of Short Exposures.—Increased definition, due probably in part to reduced frequency of movement of the respiratory and circulatory organs, and in part to absence of fogging of the photographic plate, which is inseparable from long exposures. Safety of the patient on account of the shortness of exposure to the action of the rays.

Apparatus.—The instruments employed to produce skiagraphs, with exposures varying from one to seven seconds, consist of a powerful induction coil yielding a greatly intensified secondary current, worked in conjunction with an electrolytic interrupter directly from high tension electric light mains. The core of the coil consists of transformer plates. The primary is of a much larger wire than usual and has more turns. The secondary is smaller than usual. The X-ray tube is provided with a heavy anode to withstand the current. In series with the X-ray tube, a rectifier is placed to render the current uni-directional.

Messrs. Johnson, Matthey, and Co. exhibited:—

1. Apparatus of Malleable Iridium and Rhodium.—Crucibles, dishes, &c., of malleable iridium and rhodium.

2. Apparatus of Pure Transparent Vitreous Silica.—Specimens of various forms of apparatus of fused silica, manufactured by a process which produces transparent articles of a symmetry hitherto unattained. The apparatus being *transparent*, and consisting of pure silica in a thoroughly fused and homogeneous condition, fulfils purposes for which the ordinary opaque material is unsuitable. To those unacquainted with the properties of fused silica, the following may be of interest:—It does not crack on subjection to the most violent and sudden changes of temperature. It is unattacked by the volatile acids, with the exception of hydrofluoric acid. It has a melting-point approximately equal to that of platinum. It is harder than ordinary glass. Above 1000° C. it is permeable to hydrogen and certain other gases. Its coefficient of expansion is 0·00000059 per °C. (about one-seventeenth of that of platinum). Its expansion, up to 1000° C., is regular; above 1200° C. it contracts. As far as is at present known, it shows no tendency to devitrification. Its density is 2·2 (approximately).

The Thermal Syndicate, Ltd., Wallsend-on-Tyne, showed some Pure Fused Silica Ware.—The articles consist of pure silica and are manufactured by an electric furnace process at a temperature of about 2000° C. The material is highly refractory, and possesses a very low coefficient of expansion (about one-seventeenth of that of glass), and in consequence it is able to resist sudden and extreme changes of temperature without cracking. It is unaffected by practically all acids, is an excellent electric insulator, and retains its insulating properties even at high temperatures. As will be seen it is possible to produce a brilliant lustre on the surface of the material.

CHEMICAL SOCIETY.

Ordinary Meeting, April 18th, 1907.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Messrs. W. S. Anderson and L. R. Scammiel were formally admitted Fellows of the Society.

It was announced that the Council had appointed the following Committees for 1907-1908:—

Finance Committee—E. G. Hooper, G. T. Moody, T. E. Thorpe, W. A. Tilden, and the Officers.

House Committee—W. R. Dunstan, J. E. Reynolds, W. J. Russell, J. M. Thomson, T. E. Thorpe, W. A. Tilden, and the Officers.

Library Committee—E. C. C. Baly, B. H. Brough, F. D. Chattaway, B. Dyer, A. Harden, C. A. Keene, A. Lapworth, E. J. Mills, J. M. Thomson (Chairman), J. Voelcker, J. Wade, the Editor, and the Officers.

Publication Committee—H. E. Armstrong, E. C. C. Baly, W. R. Dunstan, R. Meldola, G. T. Morgan, W. A. Tilden, J. Wade, and the Officers.

Research Fund Committee—G. T. Beilby, W. R. Dunstan, P. F. Frankland, A. D. Hall, G. Matthey, R. Messel, H. Müller, Sir A. Pedler, W. H. Perkin, W. A. Tilden, and the Officers.

Certificates were read for the first time in favour of Messrs. Hugh Hague Copping, B.A., Cabourne, Caistor, Lincolnshire; Matthewman Dalton Cowap, 21, Alma Square, St. John's Wood, N.W.; Eugen Fischer, Ph.D., Biebrich am Rhein, Germany; Walter George Gledhill, M.A., Dersingham, Greenroyde, Halifax; John Atkinson Jennings, 61, Gleneagle Road, Streatham, S.W.; Percival George Lloyd, 15, Woodside Road, Kingston-on-Thames; Harold Pochin, B.A., 12, Chapel Street, Berkhampstead, Herts; Charles Kenneth Tinkler, B.Sc., 297, Franklin Road, Kings Norton, nr. Birmingham.

A certificate has been authorised by the Council for presentation for ballot under By-law I. (Par. 3) in favour of Mr. Thomas Kirkman Dealy, Craigmin East, Magazine Gap, Hongkong.

Of the following papers, those marked * were read:—

*76. "*The Magnetic Rotation of Hexatriene*, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2$, *and its Relationship to Benzene and other Aromatic Compounds, also its Refractive Power.*" By Sir William Henry Perkin.

In a paper on the magnetic rotatory power of aromatic compounds (*Trans.*, 1896, lxix., 1025) the very high rotations they possess have been pointed out; the cause of this has been supposed to be due in the case of benzene to its ring formation, because the rotation of that substance is much higher than that of its isomeride dipropargyl.

This, however, became doubtful when it was found that *d*-$\Delta^{3:8(9)}$-*p*-menthadiene, which contains two unsaturated groupings in conjunction, gave abnormally high rotations, indicating the possibility that in benzene and other substances containing unsaturated groups in conjunction, the high rotations were also due to this circumstance. It was therefore desirable to examine some chain compound containing unsaturated groups in conjunction, in which there could be no influence due to ring formation. This was rendered possible by the examination of hexatriene, which contains three consecutive unsaturated groups.

Hexatriene was found to have a remarkably high rotation of 12·196. The difference in the formation of hexatriene and benzene is simply the difference of ring formation, due to the loss of 2 atoms of hydrogen. This affects the magnetic rotation by 0·982, and if that amount is subtracted from the above a value is obtained for the magnetic rotation of benzene, based on the assumption that benzene contains three unsaturated groupings; this amounts to 11·214.

This number is practically that actually found for benzene, 11·284, and appears to point to two conclusions, namely, that benzene contains three contiguous unsaturated groupings (Kekule's formula), and, secondly, that these have substantially the same values as in open chain compounds.

It is also noticed that the values of these unsaturated groups when in conjunction considerably increase with their number.

The refractive and dispersive power of hexatriene is very high, but the numbers do not show such a close relationship to benzene as do the magnetic rotations.

Discussion.

Mr. S. S. Pickles stated that the results obtained by Sir W. Perkin were of interest particularly to terpene chemists, who were frequently coming in contact with phenomena connected with systems of conjugated ethylenic linkings. The anomalous behaviour of compounds containing such an arrangement of double bonds called for some explanation. The fact that such compounds as phellandrene, $\Delta^{3:8(9)}$-*p*-methadiene, and $\Delta^{1:3}$-dihydrobenzene, all of which contain the grouping $\cdot C{:}C{\cdot}C{:}C\cdot$, combine with only two atoms of bromine additively, instead of with four as might be expected, and the persistence of the remaining condition of unsaturation had often led chemists to wonder what was the state of affairs in conjugated ethylenic linkings. Sir W. Perkin's determinations

had shown that from a physical standpoint there were reasons for assuming a somewhat similar condition to that prevailing in the benzene ring, and the speaker considered that the above mentioned behaviour was to some extent chemical evidence in the same direction.

Thus, accepting certain properties and behaviour as the outcome of this arrangement of double bonds, the Kekulé formula becomes applicable and explanatory in the case of benzene.

Mr. BALY pointed out that in the Kekulé benzene formula—

the conjugation of double linkings is greater than in hexatriene; in benzene this effect occurs between the double linkings *a* and *b*, between *b* and *c*, and between *c* and *a*, whilst in hexatriene, CH_2:CH·CH:CH·CH:CH_2, the effect only occurs between *a* and *b* and between *b* and *c*, and not between *c* and *a*. He asked whether this increased conjugation might not be the origin of the fact that the magnetic rotation of benzene is higher than that of hexatriene by 0·07. He did not agree with Professor Armstrong's remarks that Sir William Perkin's results do not fit in with the modern views of the benzene molecule. The three double linkings as required by the Kekulé formula give rise to a definite amount of conjugation between them, and hence to a definite magnetic rotation. If the ring be flexible and in a state of pulsation or vibration, the total amount of conjugation would remain the same, as no energy leaves or enters the system. The magnetic rotation would therefore be the same as that demanded by the three static double linkings.

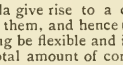
The PRESIDENT remarked that the fact that Sir William Perkin had found results which proved that the Kekulé formula for benzene is the "true" one might be interpreted as implying that the Kekulé formula is the mean of the various possible formulæ for benzene, configurations which it undoubtedly assumes during its changes.

Sir W. H. PERKIN, in reply, said that it was well to bear in mind that the difference in rotation between the chain compounds hexatriene and hexane was practically the same as that existing between the ring compounds benzene and hexamethylene. That the two classes of compounds should possess different chemical properties did not seem surprising.

The difference of 0·07 between the rotation of benzene estimated from hexatriene and the found value was small, and might partly be due to experimental error; it had therefore not been thought advisable to give any special significance to it in the meantime.

*77. "*Aromatic Azoimides.* Part I. p-*Hydroxyphenylazoimide.*" By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

The properties of camphorylazoimide have led the authors to investigate those of aromatic hydroxy-derivatives containing the N_3-nucleus in order to ascertain whether the behaviour of the first-named substance is not best explained by the constitutional formula—



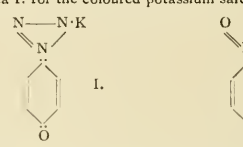
p-*Hydroxyphenylazoimide*, $HO·C_6H_4·N_3$, prepared by the action of hydroxylamine on diazotised *p*-aminophenol, is a colourless oil which has not been solidified, as an attempt to purify it by distillation under 1 mm. resulted in an explosion at 150°. The *benzoyl* derivative melts at 80°, and the *potassium* derivative has been obtained in two forms, coloured and colourless. The m-*nitrobenzoyl* derivative is faintly yellow, and melts at 118°.

Nitrous acid converts *p*-hydroxyphenylazoimide into 3-*nitro*-4-*hydroxyphenylazoimide*, $C_6H_4O_3N_4$, a volatile, orange-coloured compound melting at 91°; the *benzoyl* derivative is colourless, and melts at 103°.

DISCUSSION.

Prof. MELDOLA asked whether the identity of the benzoyl derivatives prepared, on the one hand, by benzoylating the azoimide obtained by the author's method, and, on the other, from *p*-nitrophenyl benzoate by reduction, diazotisation, and conversion into the azoimide by the usual method, did not indicate that the compound possessed the phenolic as distinguished from the quinonoid constitution.

Dr. MORGAN inquired whether the authors recognised any analogy between the isomeric potassium derivatives of their *p*-hydroxyazoimide and the two series of ethers obtained by Hantzsch and his collaborators from the nitrophenols. If such a comparison were valid the alternative Formula I. for the coloured potassium salt :—



would indicate clearly the relationship existing between this salt and the coloured ether (Formula II.) of *p*-nitrophenol.

In reply to Prof. Meldola, Dr. FORSTER stated that the benzoyl derivative of *p*-hydroxyphenylazoimide obtained from *p*-nitrophenol was slightly coloured, as indeed were most of the specimens obtained from the colourless potassium derivative of the azoimide compound, but the appearance of such specimens was quite distinct from that of the benzoyl derivative obtained from the blue salt of *p*-hydroxyphenylazoimide. He regarded Dr. Morgan's suggestion as an acceptable one, and stated that the bearing of Hantzsch's work upon the problem had been appreciated in the paper.

*78. "*Measurements of the Velocities of Saponification of the* l-*Menthyl and* l-*Bornyl Esters of the Stereoisomeric Mandelic Acids.*" By ALEXANDER MCKENZIE and HERBERT BRYAN THOMPSON.

The authors find that *l*-bornyl *d*-mandelate is saponified more quickly than is *l*-bornyl *l*-mandelate. The esters were prepared from *d*- and *l*-mandelic acids respectively, and their velocities of saponification measured in ethyl-alcoholic solution under varying conditions of concentration and temperature.

l-Menthyl *d*-mandelate and *l*-menthyl *l*-mandelate (*Trans.*, 1904, lxxxv., 1249) were also examined from the same standpoint; it was found that the former ester is the more readily saponifiable of the two.

A comparison of the velocities of saponification of the bornyl and menthyl esters shows that the former are much more quickly saponified than the latter (compare also *Trans.*, 1904, lxxxv., 378; 1905, lxxxvii., 1004).

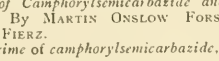
*79. "*The Constituents of the Essential Oil of American Pennyroyal. Occurrence of a Dextro-menthone.*" By MARMADUKE BARROWCLIFF.

The oil used in this investigation possessed the following characters :—$d15°/15° = 0·9297$; α_D 22 +25°44′ in a 1 dcm. tube; soluble in twice its volume of 70 per cent alcohol. It has been found to consist of—(1) an undetermined phenol, in very small amount; (2) *l*-pinene (nitroso-chloride, m. p. 103—104°; nitrolbenzylamine, m. p. 122°); (3) *l*-limonene (tetrabromide, m. p. 104°); (4) dipentene (tetrabromide, m. p. 124°), all of these terpenes being present in only small amount; (5) 1-methyl-3-*cyclo*-hexanone (oxime, m. p. 41—43°; semicarbazone, m. p. 182—183°), about 8 per cent; (6) pulegone (semicarbazone, m. p. 171°), about 30 per cent; (7) *l*-menthone (oxime,

m. p. 58—59°; semicarbazone, m. p. 184—186°), and (8) *d*-iso*menthone* (semicarbazone, m. p. 125—126°), identical with the dextrorotatory constituent of Beckmann's "inverted menthone"; the amount of these two menthones constituting about 50 per cent of the oil; (9) a sesquiterpene alcohol, about 2 per cent; (10) esters of formic, acetic, octoic, decylic, and salicylic acids, and the ester of a dibasic acid of the probable formula $C_8H_{14}O_4$, together with formic, butyric, octoic, and decylic acids in the free state; all these esters and acids being present only in small amount.

80. "*Studies in the Camphane Series.* Part XXIII. *Oximes of Camphorylsemicarbazide and Camphorylazoimide.*" By Martin Onslow Forster and Hans Eduard Fierz.

The *oxime* of *camphorylsemicarbazide*,—

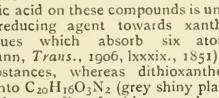


obtained from camphoryl-ψ-semicarbazide and hydroxylamine acetate, crystallises in lustrous, hexagonal plates, melts at 242°, and has $[\alpha]_D$ 105·4° in glacial acetic acid; an isomeric *oxime*, $C_{11}H_{20}O_2N_4$, produced by the action of cold dilute sulphuric acid on the foregoing substance, crystallises in lustrous needles, has $[\alpha]_D$ - 37·7° in pyridine, and melts at 222°. The *benzylidene* compound, $C_{18}H_{24}O_2N_4$, the m-*nitrobenzylidene* compound, $C_{18}H_{23}O_4N_5$, and the *furfurylidene*, compound, $C_{16}H_{22}O_3N_4$, melt at 205°, 215°, and 225° respectively.

The *oxime* of *camphorylazoimide*, $C_8H_{14}<^{CH\cdot N_3}_{C:NOH}$, melts at 84°, and, unlike camphorylazoimide itself, resists the action of cold alcoholic potash; on heating with this agent, hydrazoic acid is eliminated instead of nitrogen.

81. "*The Action of Ethyl Oxalate on Thioacetanilide and its Homologues.*" By Siegfried Ruhemann.

Homologues of dithioxanthoxalanil have been obtained by the action of sodium ethoxide and ethyl oxalate on the thioaceto-derivatives of *p*-toluidine, *m*-xylidine, and β-naphthylamine respectively. With caustic potash, they behave like dithioxanthoxalanil. The action of zinc dust and acetic acid on these compounds is unlike the behaviour of the reducing agent towards xanthoxalanil and its homologues which absorb six atoms of hydrogen (Ruhemann, *Trans.*, 1906, lxxxix., 1851), and yield colourless substances, whereas dithioxanthoxalanil is transformed into $C_{20}H_{16}O_3N_2$ (grey shiny plates which decompose at about 240°). In this case, therefore, no addition of hydrogen takes place, but the whole of the sulphur is substituted by hydrogen; the following constitutional formula is therefore suggested for the compound:—



The substance, when digested with alkalis or alkali carbonates, yields blue salts of a red compound which has not yet been carefully examined, but is probably isomeric with the reduction product, $C_{20}H_{16}O_3N_2$, of dithioxanthoxalanil. This phenomenon resembles the transformation of the yellow product of the reaction between acetylacetone and phenylpropiolyl chloride into its red isomeride, which also yields blue salts (see Ruhemann and Merriman, *Trans.*, 1905, lxxxvii., 1383).

82. "*The Action of Tribromopropane on the Sodium Derivative of Ethyl Acetoacetate.*" By Thomas Edward Gardner and William Henry Perkin, jun.

When tribromopropane reacts with the sodium derivative of ethyl-acetoacetate the principal product is *ethyl γ-bromoallylacetoacetate*, $CH_2{:}CBr\cdot CH_2\cdot CH(COMe)CO_2Et$, which distils at 120° (8 mm.), and, when hydrolysed with alcoholic potash, yields *Δγ-butinene-α-carboxylic acid* $CH{:}C\cdot CH_2\cdot CH_2\cdot CO_2H$ (m. p. 55—57°). Hydrolysis with dilute sulphuric acid converts ethyl γ-bromoallylacetoacetate into *γ-bromoallylacetone*, $CH_2{:}CBr\cdot CH_2\cdot CH_2\cdot COMe$, which distils at 83° (8 mm.), yields a liquid *oxime* and a crystalline *semicarbazone* (m. p. 150°), and when reduced with sodium and alcohol is converted into *2-hydroxy-5-hexene* (methylcrotonylcarbinol), $CH_2{:}CH\cdot CH_2\cdot CH(OH)Me$. Alcoholic potash hydrolyses γ-bromoallylacetone with elimination of hydrogen bromide and formation of *Δγ-butinene methyl ketone*, $CH{:}C\cdot CH_2\cdot CH_2\cdot COMe$. This ketone distils at 149° (749 mm.), yields an *oxime* (m. p. 48°) and a *semicarbazone* (m. p. 136°), and gives a yellow precipitate of the copper derivative when its aqueous solution is mixed with ammoniacal cuprous chloride.

The sodium derivative of ethyl methylacetoacetate reacts readily with tribromopropane, and the *ethyl methyl-γ-bromoallylacetoacetate*, $CH_2{:}CBr\cdot CH_2\cdot CMe(COMe)CO_2Et$, thus produced, yields *Δδ-pentinene-β-carboxylic acid*, $CH{:}C\cdot CH_2\cdot CHMe\cdot CO_2H$ (b. p. 207°), when it is hydrolysed with alcoholic potash.

Ethyl γγ-dibromoallylacetoacetate,—

$$(CH_2{:}CBr\cdot CH_2)_2C(COMe)\cdot CO_2Et,$$

is produced in small quantity when tribromopropane is digested with the sodium derivative of ethyl acetoacetate. It is a viscid oil which distils at 175—180° (8 mm.), and is hydrolysed by alcoholic potash with formation of *Δ•ε-heptadi inene-δ-carboxylic acid*, $(CH{:}C\cdot CH_2)_2CH\cdot CO_2H$. This acid melts at 48°, and is converted by boiling with water into *m*-toluic acid (compare *Proc.*, 1906, xxii., 133).

83. "*Indican.*" (Preliminary Notice). By Arthur George Perkin and William Popplewell Bloxam.

Indican, first described by Schunck (*Phil. Mag.*, 1885, [iv.], x., lxxiv., 74, and *Ibid.*, 1858, xv., 122), has recently (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, ii., 520) been shown by Hoogewerff and Ter Meulen to be a well-defined crystalline substance. As the result of experience gained by a study of the process of the latter chemists, the authors have devised a comparatively simple method for the isolation of this glucoside, by which a largely increased yield of the compound is obtained. The air-dried leaves of the *Indigofera Sumatrana* are extracted with acetone, the extract partially evaporated, and diluted with light petroleum which precipitates impure indican as a syrup; this after treatment with water is filtered, and the filtrate on concentration in a vacuum deposits the glucoside in a crystalline condition. The yield approximates to about 50 per cent of that extracted by the acetone, although certain precautions are necessary. This process can be carried out entirely in the cold, and the contention of Schunck (Chemical News, 1900, lxxxii., 176) that his compound was distinct from the crystalline variety is thus evidently untenable. Experiments by Hoogewerff and Ter Meulen's method (*a*) and the acetone process (*b*) have shown that the leaves of *Indigofera arrecta* also contain the same indican, but in this case the preparation is more troublesome owing partly to the presence of kaempferitrin (*Proc.*, 1906, xxii., 130), but more especially to that of a colourless sugar-like compound, m. p. 186—187°, deposited in prisms from its alcoholic solution by means of ether. It resembles dulcite, but probably has the formula $C_6H_{12}O_5$ (found, C = 43·56; H = 7·44). Numerous air-dried preparations of indican melted at 57—58°, and samples obtained through the kindness of Prof. van Romburgh, of Utrecht, and Prof. Beyerinck, of Delft, had also this property, so that the m. p. 51° of Hoogewerff and Ter Meulen may be a clerical error. When dried in a vacuum, indican fuses at about 100—101°, as stated by these chemists, but this appears to be due to the presence of water, for on further heating re-solidification ensues, the product finally melting at 176—177°. Analysis of indican dried at 100° was in agreement with the formula $C_{14}H_{17}O_6N$ (H. and t. M.) (found, C = 56·83; H = 5·83), and when dried in a vacuum and allowed to regain a constant weight in moist air the figures approximated to $C_{14}H_{17}O_6N,2\frac{1}{2}H_2O$ (found, C = 49·89; H = 6·67; N = 4·38; H_2O = 13·80).

84. "*Cupric Nitrite.*" By Prafulla Chandra Ray.

A dilute solution of cupric nitrite slowly absorbs oxygen from the air, an I is converted into nitrate, following the law of mass action. When a concentrated solution of cupric nitrite, however, is evaporated over sulphuric acid, even under diminished pressure, it partially decomposes according to the equation,—

$$3Cu(NO_2)_2 = Cu(NO_3)_2 + 2CuO + 4NO.$$

The formula assigned to basic nitrite of copper by Hampe is untenable.

85. "*The Action of Hydrogen Peroxide on Potassium Cyanide.*" By Orme Masson.

The author finds that (1) hydrogen peroxide and potassium cyanide react exothermically in aqueous solution at the ordinary temperature.

2. The peroxide is reduced without escape of oxygen so long as residual cyanide is present, but any excess of peroxide is afterwards decomposed into water and oxygen.

3. The products of the oxidation of the cyanide, which do not include oxamide or oxalate, are potassium cyanate and potassium and ammonium carbonates. Cyanate is the primary product, and tends to be converted by hydrolysis into carbonate through the catalytic agency of the peroxide.

4. A part of the cyanide is converted by hydroxysis, without oxidation, into potassium formate and ammonia.

5. The total oxidation product (cyanate plus carbonate) accounts for about four-fifths of the original cyanide, and the hydrolysis product (formate) for about one-fifth.

6. The curve representing the progress of the reduction of peroxide, so long as unchanged cyanide remains, is of the second order, and accords with the equation $\frac{dx}{dt} = k(A-x)(B-x)$, where A is the initial concentration of the peroxide, B that of the cyanide, and x the measure of the peroxide reduced, or cyanide oxidised, at time t. $B-x$ is the sum of the residual cyanide $(B-y)$, and its hydrolysed product (w).

7. The hydrolysed product (w) reaches its maximum and final value $(W = 0{\cdot}2\,B$, nearly) before the completion of the oxidising action, and thereafter the slopes of the peroxide and cyanide curves are equal. The rate of hydrolysis is expressed by the empirical rule that $\frac{dw}{dt} = k_1(A-x)(W-w)$.

8. If the solutions contain at the outset the ultimate products of the action itself, as well as fresh cyanide and peroxide, these products do not exert the influence indicated by the above equations. Hence some unknown intermediate condition probably occurs while the action is in progress.

9. The addition of caustic potash or sulphuric acid at the outset greatly retards the whole action, but the addition of ammonia has very little effect.

86. "*The Reaction between Calcium Carbonate and Chlorine Water.*" By Arthur Richardson.

The author finds that cold chlorine water decomposes calcium carbonate with formation of calcium chloride and hypochlorous acid until one part of carbonate is dissolved in thirty parts of water, as shown by Williamson, $CaCO_3 + 2Cl_2 + H_2O = CaCl_2 + 2HClO + CO_2$. At a later stage, calcium chloride, chlorate, and hypochlorite are formed, together with hypochlorous acid. This process goes on until from 40 to 50 per cent of calcium chloride is obtained; beyond this point calcium carbonate is insoluble in chlorine water.

When chlorine water containing calcium carbonate in suspension is heated, oxygen is evolved and calcium chloride and chlorate are formed. In this case also, hypochlorous acid appears to be first produced, a part being then oxidised to calcium chlorate, another part reduced to chloride, and a third part further reduced to free chlorine, whilst the hydrogen and part of the oxygen combine to form water, and the remainder of the oxygen is liberated.

87. "*The Density of Hydrogen Chloride.*" By Robert Whytlaw Gray.

Guye and Ter-Gazarian (*Comptes Rendus*, 1906, cxliii., 1233) have recently re-determined the density of this gas, and have calculated by means of it the physical atomic weight of chlorine. Some months ago the author made a series of weighings with the same object in view, but the results did not exhibit as good an agreement with each other as had been expected, and hence publication was deferred. At the request of Prof. Guye, the results of the first series of measurements are now communicated. The gas was evolved by the action of pure concentrated sulphuric acid on pure solid sodium chloride in a vacuum, and was purified by fractional distillation at a low temperature. Six experiments were made. The highest value obtained for the weight of a litre of the gas at 0° and 760 mm. in London was 1·64091 grm., and the lowest 1·64026 grm. The mean value, corrected to lat. 45, is 1·6397 grm., which is practically identical with the value 1·6398 grm. found by Prof. Guye.

88. "*Di-iodocamphor.*" By James Ernest Marsh and Robert de Jersey Fleming Struthers.

In a former paper (*Trans.*, 1905, lxxxvii., 1882), the authors stated that alkaline mercury cyanide did not form a derivative with camphor similar to that which it gives with certain other ketones. When, however, camphor is acted on by an alkaline solution of mercuric iodide containing potassium iodide, a *mercury* derivative of camphor is obtained. This substance is insoluble in water, but soluble in alcohol, and when treated with iodine gives mercuric iodide and *di-iodocamphor*. The latter substance forms brittle, yellow crystals melting at 108°, and soluble in alcohol, benzene, chloroform, or light petroleum. Its solution in chloroform is dextrorotatory. It is stable in the crystalline form, but its solution is decomposed by the action of light with separation of iodine.

89. "*Acyl-ψ-derivatives of Iminothiolcarbamic Acid and their Isomerides.*" By Augustus Edward Dixon and John Taylor.

The authors have made a further study of the additive compounds produced from acylogens and thioureas, and of the migration of acyl groups within the resultant molecules (Dixon and Hawthorne, *Trans.*, 1907, xci., 122).

Ethyl chlorocarbonate unites with phenylthiourea, yielding the hydrochloride of a feeble *base*, $NH{:}C(NHPh){\cdot}S{\cdot}CO_2Et$, carbethoxylic iminophenylthiolcarbamide (otherwise, carbethoxy-ψ-phenylthiourea), which gives a *picrate*. When liberated from its hydrochloride, the base rapidly undergoes intramolecular change, the carbethoxy-radicle exchanging places with the hydrogen of the phenylamino-group, and thus furnishing the isomeric *aa*-carbethoxyphenylthiocarbamide, $CO_2Et{\cdot}NPh{\cdot}CS{\cdot}NH_2$, m. p. 133°. The hydrochlorides from *o*- and *p*-tolythioureas yield *aa*-homologues, melting at 150° and 149° respectively.

Aryl chlorocarbonates also unite with aryl-monosubstituted thioureas; the products, on withdrawal of the halogen acid, yielding *aa*-disubstituted thiocarbamides, for example, $CO_2Ph{\cdot}NPh{\cdot}CS{\cdot}NH_2$.

Toluoyl chloride unites with thiourea and with phenylthiourea; the hydrochloride,—

$$NH{:}C(NHPh){\cdot}S{\cdot}CO{\cdot}CH_2Ph,HCl,$$

m. p. 131°, gives on treatment with calcium carbonate and alcohol the compound, $CH_2Ph{\cdot}CO{\cdot}NPh{\cdot}CS{\cdot}NH_2$, m. p. 114° (corr.), isomeric with the base, when melted, it undergoes further intramolecular change into another isomeride, $CH_2Ph{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPh$, m. p. 110°.

Attempts to isolate *aa*-benzoylphenylthiocarbamide failed, owing to the readiness with which the *ab*-form is produced. Palmityl chloride unites with thiourea and with phenylthiourea; from the latter combination, by withdrawal of the combined hydrochloric acid, *aa*-palmitylphenylthiocarbamide may be obtained.

Phenylbenzylcarbamic chloride, $CH_2Ph{\cdot}NPh{\cdot}COCl$, does not appear to yield a hydrochloride with phenyl-

thiourea, the mixture, when warmed, decomposing with formation of benzylaniline and evolution of carbonyl sulphide.

Every *aa*-disubstituted monoacyl thiocarbamide so far examined gives thiocyanic acid when treated with strong caustic alkali; the supposed bases, $NH:C(NHPh)\cdot S\cdot CO_2Me$, &c. (Dixon, *Trans.*, 1903, lxxxiii., 550), respond to this test, and hence must be regarded as *aa*-thiocarbamides.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, May 6th, 1907.

Mr. R. J. Friswell in the Chair.

"*The Works Chemist as Engineer.*" By O. Guttmann.

All chemical works have a large number of engineering problems to solve, and as a rule the chemist will have to look after them. The author explained in detail the selection of a site, the disposition of buildings and plant, the erection of buildings to standard sizes, materials, plant, &c., in view of the products to be worked and any special risks attached to them. The installation of a power-house and the many engineering details which are of advantage in the economy and control of the production of power, smoke preventers, automatic stokers and special grates, as well as water softeners and feed-water heaters, were dealt with. The utilisation and recovery of exhaust steam, the distribution of steam over the works, and precautions in laying long pipe lines were described and exemplified on some special constructions of the author. The distribution of steam from one or more central stations and the recovery of condensed water were considered. Also the transmission of power between distant buildings was discussed, and an arrangement to drive two lines of shafting at right-angles by means of belting only was shown.

The author emphasised most strongly that "works operations were not simply laboratory operations writ large." In his opinion it was useless to teach chemical technology with the help of beakers and test-tubes.

A chemist could not be expected to do all the work that he had enumerated, because only a well trained engineer with a large experience in chemical works could attempt it. On the other hand, the works chemist ought to possess an adequate knowledge of chemical technology to enable him to understand all kinds of plant, and to confer and settle details with those who have to execute it. Only the chemist who has gained practical experience as foreman of a department, and combines therewith good engineering knowledge, can be a manager in the future. To properly train a chemist, he ought to come to college better prepared and have at least four years of study, with more mechanics and physics in the beginning and a proper course of chemical technology in the end. After that it is only necessary that manufacturers should realise that a works chemist is not solely an analyst, but a highly useful practical technologist, who, given a little confidence, will in a short time repay his salary many times over.

The paper concluded with the sentences—"We have heard too much about the many chemists engaged on research in the large colour works of Germany. Highly valuable as they are, and important as their discoveries were, the German chemical industry is infinitely more indebted to that far greater number of works chemists who patiently and thoroughly investigated the manufacturing processes, who had the ability to devise improvements and economies, and who found generous manufacturers and their college trained sons to give them their confidence. It is on these lines that we must progress."

"*Apparatus for the Estimation of Carbonic Acid.*" By Herbert W. Rowell.

The sample of carbonate is decomposed by a suitable acid and boiling, and the carbon dioxide collected and weighed in potash bulbs. The apparatus consists of a 70 cc. flask with a ground-glass stopper carrying a stoppered funnel for admitting acid and subsequently air, and a bulk water-vapour trap. An air-washing tube, drying tubes, potash bulbs, and a supporting stand and aspirator complete the apparatus. It is small and neat and simply worked, and the author has regularly obtained excellent results, especially with white-lead where traces of organic matter usually present render other methods valueless.

NOTICES OF BOOKS.

Practical Agricultural Chemistry. By Frederick D. S. Robertson, F.C.S. London: Baillière, Tindall, and Cox. 1907.

A complete laboratory course of practical chemistry for agricultural students is given in this book, including the qualitative analysis of solutions containing the commoner metals and acid radicles. Separation tables are given, and the reactions of some important organic compounds are described. Gravimetric analysis and simple volumetric estimations are treated, and the more technical part of the book begins with the analysis of soils and phosphatic manures. Then feeding-stuffs, dairy products, oils and fats, sugars, tea, coffee, and cocoa, and alcoholic beverages are taken up in succession, and the book ends with the examination and analysis of water. While qualitative analysis appears to be very fully and satisfactorily treated, the part of the book devoted to the applications of chemical methods to agricultural products is marred by an indefiniteness of expression which means that the student using the book would either find it necessary to refer constantly to the teacher for fuller information, or else would waste time in gaining experience for himself by preliminary experiments. Thus, to quote only a few examples, the worker is told in the Kjeldahl-Gunning process, to boil for half-an-hour, or until all the ammonia has been driven over; but no indication is given when the latter may be assumed to have taken place, whereas the approximate measurement of the volume of the distillate is a far more satisfactory test of the complete expulsion of the ammonia even than a stated period of time. So also in the Adams coil method the coil is dried by placing it in the oven "for some time"; the flask must not be heated "too long" nor to "too high a temperature," and the temperature of distillation is not stated. The calculation of the amount of nitrogen detected by Kjeldahl's method by means of tables only, although convenient and quick, cannot be regarded as satisfactory from the students' point of view without some explanation of the way in which the figures were obtained. The neglect of such details as these must mean that either the student who uses the book is seriously hampered or the teacher is harassed by constant requests for additional information.

Science in Sugar Production. By T. H. P. Heriot Altrincham: Norman Rodger. 1907.

This book is based upon a series of articles on "Simple Methods of Chemical Control" which appeared in the *International Sugar Journal*, and were much appreciated by sugar manufacturers, more especially by those whose scientific knowledge is very limited. The author's aim is to convince the old-fashioned sugar maker that it is worth his while to begin at any rate a system of partial control, which may be regarded as a step in the right direction if the employment of a skilled chemist is impossible, and with the requirements of such a manufacturer kept in view he enters into details of the simplest methods, which almost anyone could use with a fair degree of accuracy. The fitting up of a laboratory and the use of a balance are described for the novice, and directions for simple chemical

and physical processes, such as making up a solution to a given strength and finding densities, are explained. The determination of sucrose by means of a polariscope is treated more fully, the author condemning a mere rule-of-thumb knowledge of its use as quite insufficient for the sugar maker, whether he is a chemist also or not. Consequently, the somewhat difficult subject of polarisation is clearly discussed, and the construction and use of the instrument are explained from a theoretical as well as from a practical point of view. The book should fulfil its purpose satisfactorily, and the practical sugar maker will find it a useful and trustworthy guide.

Industrial Alcohol. By JOHN GEDDES M'INTOSH. London: Scott, Greenwood, and Son. Toronto: Copp Clark Co., Ltd. New York: D. Van Nostrand Co. 1907.

IN this book the production and uses of alcohol are discussed in a most comprehensive spirit, and the author shows a wide acquaintance with its manufacture and applications. Fully illustrated accounts are given of its preparation from beets, grains, potatoes, wine, and sugar-cane, and the plant necessary for distillation is described in detail. The manufacture and uses of various substances derived from alcohol, such as ether, chloroform, and amyl alcohol, are treated comparatively shortly, and two chapters deal with the use of alcohol in the arts, crafts, and industries, as well as for lighting, heating, and motive power. The author is evidently thoroughly familiar with the processes and machinery employed on the Continent, and he places at the disposal of his readers in a very convenient form a knowledge which has been acquired from all sources, while his suggestions in the direction of economy by the reduction of working expenses are well worth the attention of every distiller.

The Workmen's Compensation Act, 1906. With Notes. By W. ADDINGTON WILLIS, LL.B. (Lond.). Ninth Edition of "Willis's Workmen's Compensation Acts." London: Butterworth and Co.; Shaw and Sons. 1907.

THE Workmen's Compensation Act of 1906 is so far-reaching in its provisions that the ninth edition of this book will be welcomed by the general public, and all employers of labour should not fail to get a copy. The Act is clearly explained in it, and notes are added containing detailed accounts of all cases decided under the original acts which are equally applicable to the new statute.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 16, April 22, 1907.

Hydrogenation of Isocyanates.—Paul Sabatier and A. Mailhe.—By the method of direct hydrogenation with reduced nickel, the authors have transformed two isocyanates—one belonging to the fatty and the other to the aromatic series. 1. *Ethyl Isocyanate.*—The vapours of this body were passed over nickel with excess of hydrogen at 180—190°, and the resulting substances formed a strong aqueous solution in a cooled receptacle; by distillation the following fractionations were obtained:—(i.) A little ethylamine, boiling at 18°; (ii.) a considerable weight of methylethylamine, boiling at 35°; (iii.) a certain amount of diethylamine, boiling at 60°; (iv.) a little triethylamine, passing over at 90°. The principal reaction is therefore the normal process of hydrogenation, giving rise to methylethylamine, $C_2H_5.N:CO + 3H_2 = H_2O + NH{<}\begin{matrix}CH_3\\C_2H_5\end{matrix}$. The presence of the other amines is explained by the fact that the water produced reacts with part of the ethyl isocyanate to give diethyl urea, $(C_2H_5.NH)_2CO$, which also undergoes hydrogenation: $(C_2H_5.NH)_2CO + 3H_2 = H_2O + C_2H_5.NH_2 + NH{<}\begin{matrix}CH_3\\C_2H_5\end{matrix}$.

2. *Phenyl Isocyanate.*—Hydrogenation is carried out as in the preceding case, and white crystals of diphenyl urea are obtained, melting at 237°. This is produced by the action of water formed in a primary stage of the reaction:—

$$C_6H_5.N:CO + 4H_2 = C_6H_5.NH_2 + CH_4 + H_2O \rightarrow$$
$$\rightarrow 2(C_6H_5.N.CO) + H_2O = CO_2 + (C_6H_5.NH)_2CO.$$

Hence, in this case hydrogenation does not proceed in the normal manner.

A New Silicide of Tungsten, Si_2W.—Ed. Defacqz.—Hitherto only one compound of silicon and tungsten, Si_3W_2, has been isolated. The author describes the preparation of a new silicide, Si_2W. There are two methods of preparation:—1. By heating copper silicide with amorphous tungsten in the electric furnace. The resulting mass is treated with dilute nitric acid, then with dilute soda, till finally a crystalline deposit is left. 2. An intimate mixture of silica, tungstic anhydride, flowers of sulphur, and powdered aluminium is placed in a crucible, covered with powdered magnesium, and ignited according to the alumino-thermic method; after cooling, crystals of Si_2W are then produced. The analysis of this compound, which proved a delicate and difficult task, gave the following results:—

	1.	2.	3.	4.	Calculated for Si_2W.
Silicide ..	24·08	24·03	24·32	23·66	23·34
Tungsten .	74·91	75·46	75·20	76·06	76·66

Properties.—Si_2W consists of brilliant prismatic needles of a clear grey colour; density, 9·4 at 0°; chlorine attacks it readily towards 450°, to give silicon chloride and tungsten hexachloride; it remains unaltered when heated in air up to 900°, copper decomposes it towards 1200°; the ordinary acids and aqua regia have no effect upon it, a mixture of nitric and hydrofluoric acids attacks it violently; the fused alkalis convert it into the alkaline tungstates and silicates.

MISCELLANEOUS.

Apparatus of Pure Iridium and Rhodium.—Messrs. Johnson, Matthey, and Co., Ltd., have succeeded in producing iridium and rhodium of such extreme purity as to render these hitherto practically unworkable metals so malleable as to enable their being used for the manufacture of such apparatus as basins, tubes, and flasks. These metals having a very high melting-point, and being almost unattacked by acids, will doubtless prove of great value in chemical research.

Apparatus of Fused Silica.—The scientific work of which the process of manufacturing this apparatus is the outcome, was carried out by two eminent English scientific men about ten years ago; unfortunately, as so often happens in these cases, its commercial importance was first recognised in Germany, and its production on an industrial scale commenced, little or nothing of a similar nature being attempted at home. An English firm has now taken up the original process, and by suitable modifications to meet industrial requirements are now enabled to place this material upon the market at a price which can no longer be considered prohibitive. The apparatus is manufactured from the purest silica obtainable. At a high temperature this substance melts and yields a viscid liquid which can by suitable means be fashioned into apparatus having all the appearance of ordinary glass. It possesses

many properties which are likely to render it of immense service both to science and to industry, *e.g.*, it can be heated white hot and plunged into water, or otherwise rapidly cooled, without any danger of cracking; it is quite unattacked by water or acids, ordinary glass under similar conditions being appreciably dissolved.

Royal Institution, Albemarle Street.—On Saturday, May 18, at 3 o'clock, Mr. Arthur Bourchier delivers the first of two lectures at the Royal Institution on "The Limits of the Dramatic Art," and on Thursday, May 23, at 3 o'clock, Professor Sir James Dewar commences a course of three lectures on "Chemical Progress—Work of Berthelot, Mendeleeff, and Moissan." The Friday Evening Discourse on May 24 will be delivered by Professor J. A. Fleming, on "Recent Contributions to Electric Wave Telegraphy"; and on May 31 by Mr. A. H. Savage Landor, on "Recent Journey Across Africa."

Osmium.—C. Paal and Conrad Amberger.—To obtain colloidal osmium preparations alkaline osmiate solutions were reduced by hydrazine hydrate in presence of protalbinic or lysalbinic acid sodium, but the reaction did not take place quantitatively, and the product was not elementary osmium, but an oxide or oxide-hydrate approximating in composition to the dioxide with 14·35 per cent of oxygen. To determine the osmium in these colloidal preparations the substance was ignited in oxygen, when the tetroxide was formed. This was collected in caustic potash containing alcohol, or in dilute alcohol, and the osmium in the solution of potassium osmiate or colloidal osmium tetroxide determined. As all known methods of determining osmium quantitatively have proved more or less inaccurate, the authors tried to estimate it by the direct precipitation of potassium or sodium osmiate solution, obtained by dissolving the tetroxide in aqueous alkali solution containing alcohol, by means of dilute sulphuric acid. This method gave accurate results. Formaldehyde reduces alcoholic solutions of osmium tetroxide to the dioxide, and alcohol reduces it to the hydroxide, $Os(OH)_4$; this colloidal reduction product begins to separate out after the liquid has stood for about five or six hours, and its formation may be hastened by warming. This method may be used for the quantitative estimation of osmium. Hydrazine hydrate reduces osmium tetroxide dissolved in alcohol to a product which contains approximately the same amount of oxygen as the compound OsO, but it is possibly a mixture of osmium with higher oxides.—*Berichte*, xl., No. 6.

MEETINGS FOR THE WEEK.

Tuesday, 21st.—Royal Institution 3. "Alfred Stevens, the English Sculptor and Painter," by D. S. MacColl.

Thursday, 23rd.—Royal Institution, 3. "Chemical Progress—Work of Berthelot, Mendeleeff, and Moissan," by Prof. Sir James Dewar, F.R.S., &c.

Friday, 24th.—Royal Institution, 9. "Recent Contributions to Electric Wave Telegraphy," by Prof. J. A. Fleming, F.R.S.

Saturday, 25th.—Royal Institution, 3. "The Limits of the Dramatic Art," by Arthur Bourchier, M.A.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2478.

REACTION BETWEEN TITANIUM TETRACHLORIDE AND ETHER.

By HENRY R. ELLIS, B.Sc.

In an attempt to prepare organic compounds of titanium by replacing the chlorine atoms of titanium tetrachloride by alkyl radicals through the agency of Grignard's reaction, it was observed that the ether used to dissolve the magnesium alkyl halide reacted with the titanium tetrachloride.

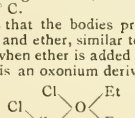
Titanium tetrachloride (45 grms.) was placed in a Wurtz flask, the side tube of which passed into a Liebig condenser connected to a receiver standing in a freezing mixture.

The flask itself was surrounded by ice. A tap funnel was inserted into the neck of the Wurtz flask, and from this pure anhydrous ether free from alcohol was allowed to drop very slowly on to the titanium tetrachloride.

The flask and its contents were shaken frequently during the reaction; as soon as the ether came in contact with the titanium tetrachloride a bright yellow crystalline solid began to separate, and continued to do so until the whole mass set solid.

About 50 cc. of ether was added before the whole of the liquid disappeared (two and a-half hours); no gas or ether passed through the condenser, and nothing collected in the receiver in the freezing mixture, although this was at a temperature of -12° C.

It seems from this that the bodies produced are double compounds of $TiCl_4$ and ether, similar to the white crystalline body produced when ether is added to tin tetrachloride and which probably is an oxonium derivative—



No such body was produced when silicon tetrachloride was added to ether.

The yellow crystalline mass had the appearance of rhombic sulphur deposited from carbon bisulphide.

The substance was next warmed up on a water-bath, and became liquid at about 30° C., but on cooling solidified again, except about 2 cc. of a dark brown viscous liquid which became solid on the addition of about 2 cc. of ether; during the warming no liquid condensed in the receiver.

The solid was allowed to stand twenty hours, and was then fractionally distilled—the first fraction (3 cc.) was collected up to 34° C., and consisted of ether, hydrochloric acid gas, and a small quantity of a yellow liquid which crystallised out.

The second fraction was collected up to 60° (30 cc.), and consisted of a yellow oil which quickly solidified to yellow gem-like crystals, the thermometer quickly rose to 160° C., and about 20 cc. of a yellow liquid was collected which rapidly solidified to a mass of small yellowish white crystals. Another distillate was collected from 170° to 196° (5 cc.), and consisted of orange crystals of melting-point about 70° C.

The residue in the flask consisted of a brown powder similar in appearance to hydrated oxides of manganese.

This residue was quite insoluble in pure dry ligroin, whilst all the other bodies were becoming less soluble with increase of boiling-point. A portion of this body was washed with ligroin and dried, and the chlorine and titanium estimated; the titanium was estimated by igniting a weighed amount in a crucible after treatment with strong nitric acid, and weighing as TiO_2; the chlorine was estimated by boiling with water until all the gelatinous precipitate obtained was broken up, neutralising and titrating with N/10 $AgNO_3$. Ti = 34·4 per cent, Cl = 18 per cent.

The other substances, although they do not fume in the air, slowly decompose on standing, with evolution of hydrochloric acid gas and ethyl chloride, and have not yet been analysed.

The Chemical Laboratory,
The Polytechnic, Regent Street.

THE SO-CALLED "INFUSORIAL EARTHS" AND THEIR CHEMICAL ANALYSES.

By Prof. ARTHUR M. EDWARDS, M.D.

I believe in going to the bottom of anything when examining it. I believe in making a microscopic examination as well as a chemical examination when we examine anything. I use the microscope when I can; I use chemical analyses also.

It is interesting as well as important to compare the chemical analyses of the so-called "infusorial earths" which contain the shells of Bacillaria. They are popularly known as "diatom earths," but they are Bacillarian now. I find the records of the following:—

Hofmann (*Journ. Prakt. Chem.*, 1864) gives the analysis of the earth from Bohemia.

	1.	2.	3.	4.
Ammonia	0·03	0·01	0·34	
Potash	0·02	0·30	0·24	0·40
Soda	0·30	Trace	Trace	
Magnesia	—	0·43	0·36	0·05
Lime	0·41	0·44	0·64	Trace
Alumina, ferric oxide	0·81	5·40	5·60	0·91
Sulphuric acid	0·12	Trace	0·54	—
Phosphoric acid	0·24	Trace	Trace	0·19
Organic matter	4·20	1·30	13·20	15·45
Water	13·30	10·90	7·00	6·00
Silica	74·20	80·30	72·60	77·00
	99·63	99·08	100·52	100·00

It is from Kutschind, near Bilin, Meistersdorp, Luisa Spring, in Fransbad. No. 1 is from the upper layer, Bilin; No. 2 is from the lower layer, Bilin; No. 3 is from the Meistersdorp; and No. 4 is from Franzenbad.

These are all from "the iceberg period" geologically. No. 1 of the "tripoli," as it is called, has a density of 1·862; No. 2, of 1·944—that is to say, it is nearly twice as heavy as water.

In the "Kieselguhr zu Franzenbad" Ehrenberg discovered, in 1838, what he called *Cocconeis* (?) *clypeus*. It was afterwards, in 1841, called *Camphylodiscus clypeus*, and was also found at Santa Fiore, Italy. This also belongs to "the iceberg period." He also found in the Franzenbad deposit *Navicula bohemica* and *N. sculpta*. These are both varieties of *N. amphisbæna* of Bouy de St. Vincent, 1826. Ehrenberg calls it *N. ventricosa* (1830), and Kützing calls it *Frustulia depressa*. It is not a *Navicula*, but a *Neidium* of Pfitzer; it should be *Neidium amphisbæna*, B. de S. V.

W. Habirshaw analysed the "electro-silicon" of Virginia City, Nevada, and found it to contain—

Silica	81·08
Water, volatile at a red heat	18·44
Loss	0·48
	100·00

This belongs to the Eocene period, before the Oligocene Tertiary period. The Oligocene period is now, in this country (United States), the Neocene period or formation,

The California infusorial stratum, which was discovered by Bailey at San Pablo, near San Francisco, and near by and upon the stratum I lived nearly two years, and the Monterey and Santa Monica, is Oligocene, though ranked as Miocene by most geologists. Of course it is the Neocene period or formation now.

Cooke gives an analysis of the Drakesville, New Jersey, "infusorial stratum," which is as follows:—

Silica	80·66
Alumina	3·84
Lime	0·58
Loss on ignition (organic matter and water)	14·01
	99·09

The Drakesville deposit presumably belongs to "the iceberg period."

In Mexico, near Socorra, within 12 miles of the city, is a vast layer of infusorial earth which belongs to the Eocene period also. It seems to belong to the Occidental Sea, but has not been investigated as yet.

Now we see that the Eocene formation does not contain any alumina, and is not a clay, strictly speaking. But the iceberg period strata, both in Bohemia and in New Jersey, are clays made by the breaking down of the granite. This is the difference between those from the Eocene and the Iceberg strata, and it has been rendered solid by the solution of the silica and not by the clay.

I do not know any of them except that from Franzenbad, which has been analysed. This is also known as Soos; it contains, too, a large quantity of *Camphylodiscus*. In the Eocene period of Utah lake, and of Mono lake, and of Pyramid lake, there is present a *Surirella utahiensis* of Ehrenberg; but this is *Surirella striatula* of Turpin (1828). It is *Navicula* (?) *striatula* of Ehr., but it is a true *Surirella*. *Surirella striatula* living is brackish and marine. It is also fresh water in "Kieselguhr von Franzenbad." In fact, it sometimes occurs circular instead of elongated, and looks as if it were passing into *Camphylodiscus*. Formerly *Camphylodiscus clypeus* was known as a fossil form alone, and occurs in fresh water only. But now it is known as a brackish form in the North Sea, and there recent. It is rare in what I have called the Raised Coast period, but this is Upper Eocene as now placed, of Newark, N.J.

Dall (U.S. Geological Survey, 1892, *Bull.* No. 34, p. 117) gives an analysis by Prof. F. W. Clarke of Bailey's infusorial stratum at Ballast Point, Hillsboro County, Florida, as follows:—

Silica	70·78
Alumina and iron	11·33
Lime	2·18
Water and loss	15·71
	100·00

He says:—"An examination of this marl by Mr. Lewis Woolman, the well-known student of microscopic organisms, did not reveal a single diatom." Mr. Woolman sent me specimens of the marl, in which I also failed to observe the diatoms. Since then I have received some from Manetee, Florida, which is about 35 miles south of Tampa, Florida, and for which I am indebted to Mr. C. M. Cunningham, of Mobile, Alabama, and to Dr. W. B. Ward, of Poughkeepsie, New York, which showed Bacillaria undoubtedly, but in a fossil condition. The fossil Bacillaria, that is to say dug from the ground in distinction from those which are living (recent), are of a marine condition; that is to say, they live in the ocean, and belong to the Myocene or Oligocene tertiary period. This has been formed into the Upper Neocene period of formation now. They have not been detected on the Atlantic side of Florida, Georgia, South Carolina, or North Carolina, nor yet in Alabama, Louisiana, nor in Texas or Mexico, but we may suppose it possible: they will be found there I am sure. I am only waiting for an opportunity to visit these localities myself, for now I am convinced that the fossil Bacillaria can only be found by what is called a "diatomaniac," a person who is crazy over diatoms or Bacillaria, in which category I am proud to be known. The fossil Bacillaria of Newark, New Jersey, were found by myself, although travelled over hundreds of times by dozens of students, and I only found them when my attention was especially fixed by them and when I had time to look at them.

In the *Bulletin* of the Department of Geology of the University of California, 1893, is an article by Professor Andrew C. Lawson on the Geology of Carmelo Bay in California, wherein he speaks of the Monterey series, meaning the light coloured rocks which contain the Bacillaria, and of which I have spoken, on the Pacific coast of California. He gives the results of a chemical analysis as follows:—

Silicic oxide	86·89
Aluminium oxide	2·32
Ferric oxide	1·28
Calcium oxide	0·43
Magnesium oxide	Trace
Potassium oxide	1·26
Sodium oxide	2·32
Ignition	4·89
	99·39

But this immediate specimen contained no bacillarian remains, and it is interesting to remark that Prof. Lawson, although classifying the rocks as Miocene, says:—"The infusorial beds at Monterey appear, therefore, to be exceptional, and not representative of the series as a whole." And it is suggested that perhaps the microscopic examination of the Monterey shale will show, as a geological analysis shows, that it is of volcanic origin, and that we do not understand the geology of these rocks. I suggest the recent elevation of these rocks from the sea bottom, modified of course by volcanic agency; they then become, as they are now when microscopically examined, the same as were brought home by the *Challenger* and *Tuscarora*, as I have shown.

The analysis of the Raised Coast period clay was made by Prof. B. Silliman, and published by Prof. J. W. Bailey in a paper entitled "Notice of some New Localities of Infusoriæ, Recent and Fossil" (*Am. Journ. Sci.*, 1844, xlvii., 337). He examined the blue clay from New Haven, perhaps the same as the Quinipiac marshes, in which W. A. Terry has described diatoms (Bacillaria). Being used as a fertiliser an analysis was made. When magnified, it was found to contain particles of quartz, hornblende, and felspar, derived from the rock granite of the Green Mountains which were brought down by the glacier when it was formed, in the Glacial period; in fact, I believe these clays were formed then or antecedent thereto.

There were seen the following Bacillaria:—

Actinocyclus senarius.
Coscinodiscus excentricus.
Coscinodiscus oculus-iridus.
Cocconeis oceanica.
Dicladia (?)
Ennolia westermannī.
Galionella (*Melosira*) *sulcata.*
Grammatopha oceanica.
Pinnularia peregrina.
Pinnularia lyra.
Pinnularia didyma.

(These last three are now all Naviculas. I quote Bailey's original list).

Raphoneis rhombus.
Tessela catena.
Dictyocha speculum.
Dictyocha fibula.
Spongiolithis caput-sepertensis.

The analysis was—

Silica	58·633
Alumina	30·563
Oxide of iron	6·186
Carbonate of lime	5·263
Magnesia	0·705
	100·350

So it is an aluminium and iron silicate. When we compare the analysis of this clay with other infusorial clay, as at Richmond (Virginia), Monterey (California), &c., and with the "diatom ooze" of the Atlantic and Pacific oceans, they are found to be the same microscopically and chemically.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part II.—Analysis of the Silver, Copper, and Tin Groups.

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 221).

Analysis of the Copper Group (continued).

Procedure 26.—To the HNO_3 solution (P. 23) add 2 to 3 cc. concentrated H_2SO_4, and evaporate in a casserole until fumes of H_2SO_4 begin to come off. Cool and pour into 10 to 15 cc. cold water, rinsing out the casserole with the same solution. Cool again, shake, and allow the mixture to stand five minutes, but not much longer. (Finely divided white precipitate, presence of *lead*; but a coarsely crystalline precipitate may be due to bismuth). Filter and wash the precipitate with H_2SO_4 (1·20), and finally with a little water. (Precipitate, P. 14, to confirm the presence of lead; filtrate, P. 27).

Notes.

1. $PbSO_4$ is somewhat soluble both in water and in concentrated H_2SO_4, but much less so in moderately dilute H_2SO_4, its solubility being scarcely appreciable in mixtures containing one volume of H_2SO_4 (1·84) and two to six volumes of water. That the solubility in dilute H_2SO_4 is less than that in water is due mainly to the common ion effect. Concentrated H_2SO_4 is, of course, an entirely different solvent. $PbSO_4$ dissolves fairly readily in dilute HNO_3 (or in dilute HCl), owing to metathesis arising mainly from the tendency to form un-ionised H_2SO_4; hence, although this effect of HNO_3 is partly counteracted by the presence of much H_2SO_4, yet, to ensure complete precipitation of $PbSO_4$, the HNO_3 must be removed by evaporation.

2. When much bismuth is present it ordinarily is dissolved at first when the water is added to the concentrated H_2SO_4, provided the mixture is kept cold; but from this solution a coarsely crystalline precipitate of an oxysulphate, such as $(BiO)_2SO_4$, separates slowly upon standing in the cold but almost immediately upon heating, and to such an extent that there may remain in solution not more than 50 mgms. of bismuth. If such a precipitate has separated with the $PbSO_4$, filter, treat the filtrate by P. 27, and dissolve the precipitate by pouring repeatedly through the filter a 5 to 10 cc. portion of HCl (1·12), and test the solution so obtained for lead by following P. 26 and P. 14.

Procedure 27.—To the H_2SO_3 solution (P. 26) add NH_4OH slowly until a strong odour of it persists after shaking. (White precipitate, possible presence of *bismuth*; blue solution, presence of *copper*). Shake to cause coagulation, filter, and wash the precipitate. (Precipitate, P. 28; filtrate, P. 29 and 30).

* From the *Technology Quarterly*, xix., No. 3, September, 1906.

Notes.

1. The precipitate produced by NH_4OH may also consist of $Fe(OH)_3$, or of other hydroxides of the iron group, if these elements were carried down in the H_2S precipitate or were not completely removed from it by washing. The formation of a small precipitate is, therefore, not a sufficient proof of the presence of bismuth, and the confirmatory tests must be applied. Antimony which, like bismuth, gives with water a precipitate of an oxychloride cannot be present in sufficient quantity to be precipitated by NH_4OH.

2. That $Cd(OH)_2$, or $Cu(OH)_2$, though only very slightly soluble in water, dissolves in NH_4OH is due to the conversion of the Cd++ or Cu++ ion in the saturated solutions into the complex cation $Cd(NH_3)_4$++ or $Cu(NH_3)_4$++, which is formed by combination of the simple ion with un-ionised ammonia. These complex cations have an extremely small ionisation tendency; thus for cadmium in a normal NH_4OH solution the ratio of the concentration of the complex to the simple ion is about 10^7. The solubility of these hydroxides in NH_4OH is greatly increased by the presence of ammonium salts, since these salts, owing to the common ion effect, greatly reduce the ionisation of the NH_4OH, and therefore the OH^- concentration in the solution, thus enabling the Cd++ or Cu++ concentration, and therefore also the corresponding complex ion concentration, to attain a much larger value than in the saturated solutions of $Cd(OH)_2$ or $Cu(OH)_2$, in NH_4OH alone. It will be noticed that four distinct equilibria are involved—that between solid $Cd(OH)_2$ or $Cu(OH)_2$ and its ions; that between Cd++ or Cu++, NH_3, and $Cd(NH_3)_2$++ or $Cu(NH_3)_4$++; that between NH_4OH, NH_3, and H_2O; and that between NH_4OH, NH_4^+, and OH^-. It may be further mentioned that, since in any dilute solution the concentration of the water is substantially constant, the concentration of any hydrate (like NH_4OH) is proportional to that of the anhydrous substance (NH_3).

Procedure 28.—Dissolve the NH_4OH precipitate (P. 27) by pouring a little HCl (1·12) through the filter, evaporate off the acid almost completely, leaving the residue only barely moist with it, add 1 to 2 cc. water, pour the solution into a flask containing 100 cc. water heated to 50—70°, and allow the mixture to stand two or three minutes. (White precipitate, presence of *bismuth*). Filter, wash once, and pour through the filter a freshly prepared solution of sodium stannite. (Black residue, presence of *bismuth*).

Notes.

1. The white precipitate formed in the first confirmatory test for bismuth is BiOCl, which is produced by the hydrolysis of $BiCl_3$. If HCl, the other product of the hydrolysis, is present in the solution, the reaction will not be complete, and a greater or less quantity of bismuth will remain in solution and thus escape detection. This quantity increases rapidly with the acid concentration in accordance with the law of mass action. For this reason, if the presence of half a milligrm. of bismuth in the precipitate is to be detected, the HCl must be removed by evaporation so completely that not more than 0·2 cc. remain, and the solution must be added to a large volume of water. Warm water is used, because the precipitation of BiOCl takes place more rapidly at the higher temperature.

2. The solution of sodium stannite (Na_2SnO_2) is prepared when needed by adding a 10 per cent NaOH solution to a 10 per cent $SnCl_2$ solution until the $Sn(OH)_2$ first formed is dissolved. The solution must be freshly prepared, because it decomposes spontaneously into sodium stannate (Na_2SnO_3) and metallic tin, and because it oxidises in contact with air to sodium stannate. SnO_2H_2 is an example of a so-called amphoteric substance—one which acts either as a base or an acid, as is shown by its solubility in both acids and alkalis.

3. The final test with sodium stannite depends on the reduction of BiOCl to black metallic bismuth. The test is an extremely delicate one, and by it may be detected a quantity of bismuth so small as to produce only a scarcely visible turbidity of BiOCl; for, when the precipitate in such a solution is collected on a filter and treated with stannite, the black colour of the bismuth is very apparent. Antimony oxychloride, even if present, is not blackened by the stannite. The NH_4OH precipitate itself might be directly tested with this reagent; for the other reducible substances, like $Fe(OH)_3$, $Pb(OH)_2$, or $Cu(OH)_2$, that might possibly be present in that precipitate are not reduced by short contact with stannite solution in the cold. It is, however, often desirable to get the double indication of the presence of bismuth, as furnished by the precipitation of the oxychloride by water and by its blackening with the sodium stannite.

Procedure 29.—Acidify one-fourth of the NH_4OH solution (P. 27) with acetic acid, add 2 to 3 drops 3 per cent $K_4Fe(CN)_6$ solution, and allow the mixture to stand for several minutes. (Red precipitate, presence of *copper*). If it is uncertain whether there is a precipitate, pour the solution through a filter and wash with a little water. (Pink colour on the filter, presence of *copper*).

Notes.

1. The confirmatory test for copper depends on the precipitation of red cupric ferrocyanide, $Cu_2Fe(CN)_6$. Since this test is a more delicate one than the formation of a blue colour with NH_4OH (P. 27), it should be tried even when the NH_4OH solution is colourless. Cadmium is also precipitated by $K_4Fe(CN)_6$; but the precipitate is white, and does not prevent the pink colour of the copper compound from being detected, provided only a small quantity of $K_4Fe(CN)_6$ is added; for the copper salt, owing to its smaller solubility, is first precipitated.

2. Nickel, like copper, gives a blue solution with excess of NH_4OH; but even if present it would give a greenish white, not a red precipitate, with $K_4Fe(CN)_6$. Aside from copper, only the rarer elements uranium and molybdenum give red precipitates with this reagent; but they do not do so in an acetic acid solution, such as is obtained in the procedure.

Procedure 30.—To the remainder of the NH_4OH solution (P. 27 and 29) add solid KCN till the blue colour disappears, and pass in H_2S gas for about half a minute. (Flocculent yellow precipitate, presence of *cadmium*). (Precipitate and solution, reject).

Notes.

1. By the addition of KCN the copper salt is reduced from the cupric to the cuprous state and then combines with the excess of KCN to form the complex salt $K+Cu(CN)_2-$ (potassium cuprocyanide). This result is due to the fact that cupric cyanide tends to decompose spontaneously into cuprous cyanide and cyanogen, and that this reaction takes place completely in KCN solution, owing to removal of the cuprous cyanide by combination with the excess of KCN. In the presence of NH_4OH the cyanogen is not evolved as a gas, but reacts with it, forming cyanate (NH_4CNO) and cyanide and other more complex products. The fact that neither CuS nor Cu_2S is precipitated from this solution by an alkaline sulphide shows that neither the Cu^{++} nor $Cu+$ concentration is sufficient to cause the value of the solubility product to be attained. The extremely small $Cu+$ concentration is due to the very slight ionisation tendency of the complex anion $Cu(CN)_2-$: thus it has been estimated that in a normal KCN solution the ratio of the concentration of the complex anion to that of the simple $Cu+$ ion is about 10^{26}.

2. The cadmium ammonia salt is also converted by KCN into a complex cyanide, namely, $K+_2Cd(CN)_4=$ (potassium cadmicyanide), since its complex anion has a much smaller ionisation tendency than the cation $Cd(NH_3)_4++$; thus in a normal KCN solution the ratio of the concentration of the complex anion to that of the simple $Cd++$ ion is about 10^{17}. Yet this complex anion is sufficiently dissociated into $Cd++$ ion to cause the solution to become saturated with CdS when an alkaline sulphide is added.

3. A very small black precipitate (which may be due to HgS or PbS) may sometimes be produced in the final test for cadmium with H_2S; but, provided the analysis has been properly conducted, not in sufficient quantity to prevent the yellow colour of 1 or 2 mgrms. of CdS from being seen. In case a black precipitate is produced, and thus prevents a positive conclusion as to the entire absence of cadmium, the precipitate may be treated, in order to eliminate the black sulphide, as follows:—Boil the precipitate for about five minutes with about 15 cc. of a mixture of one volume of H_2SO_4 (1·20) with four volumes of water, filter, cool the filtrate, add to it three times its volume of water, and pass H_2S into it for five to ten minutes. A yellow precipitate of CdS should then be obtained, if cadmium is present.

(To be continued).

THE ACTION OF SODIUM ON ACETONE.*

By RAYMOND FOSS BACON and PAUL C. FREER.

A number of years ago one of us described the action of sodium on acetone (*Am. Chem. Journ.*, 1890, xii., 355), showing that in the presence of absolute ether a *white* sodium derivative is obtained which has 30·17 per cent of sodium (calculated for sodium acetone 28·75 per cent) and which, on being added to dilute hydrochloric acid, regenerates acetone. Subsequently (*Am. Chem. Journ.*, 1891, xiii., 320), in a second discussion of the subject, it was demonstrated that hydrogen is evolved when sodium acts on acetone, and the resulting sodium derivative is again described as being *white*, but *turning red* rapidly on exposure to air and moisture. It was also shown that when this sodium derivative is added to dilute hydrochloric acid and *repeatedly extracted with ether*, no condensation products of acetone (or at least only traces) could be isolated. The sodium derivative therefore does not contain these condensation products to any great extent. The mother liquors from a number of operations in the preparation of sodium-acetone were carefully retained, united, washed with water, extracted with ether, and the residue distilled, a very small quantity of mesityloxide and some higher condensation products of acetone being isolated. Again, in another discussion of the subject (*Am. Chem. Journ.*, 1893, xv., 585; *Liebig's Ann. Chem.*, cclxxviii., 116), by acting on sodium under xylene, with acetone, 62·7 per cent of the theoretical amount of hydrogen was obtained (this observation was subsequently confirmed by Beckmann and Schleibs (*Liebig's Ann. Chem.*, 1896, cclxxxix., 86), and in the same paper, in discussing the preparation and analysis of the sodium derivative of acetone, it was shown that delay during the preparation of this derivative always resulted in increasing the percentage of sodium. A large number of samples of acetone-sodium were prepared, decomposed by dilute, ice-cold acetic acid, and united until a sufficient amount had been collected to study the reaction products; acetone (isolated as the sodium-bisulphite compound), isopropyl, and ethyl alcohols were identified among these; under favourable circumstances as much as twice the quantity of acetone as compared with isopropyl alcohol was isolated. The high-boiling fractions from the separation of the above substances gave pinacone, a small quantity of phoron, and, presumably, reduction products of the latter. *Mesityloxide could not be isolated.* A portion

* From the *Philippine Journal of Science*, ii., No. 1.

of the reaction product of sodium on acetone was found to be soluble in ether; this on careful evaporation gave a yellow powder, which oxidised in the air with remarkable readiness. (Our work shows that, under proper conditions, this residue is white.) This residue, on acidifying, separates some oil, which was isolated, and the presence of acetone was afterwards proven in the solution. The high-boiling portion of the residue was phoron. These high-boiling oils *react rapidly with phenyl hydrazine*. No isopropyl alcohol and but very little pinacone can be found among the products of decomposition of this soluble portion obtained by the action of sodium on acetone, but by far the greater part of the condensation products produced by the action of sodium on acetone are found in this residue. In proportion as such condensation products are produced, the percentage of sodium in sodium acetone will be increased.

In the *Journal of the Chemical Society*, 1906, lxxxix., 1258, Millicent Taylor has returned to the subject and comes to the remarkable conclusion that acetone-sodium "consists chiefly of caustic soda mixed with a small proportion of the sodium derivatives of alcoholic reduction and condensation products of acetone."

Apart from the fact that in her discussion Miss Taylor completely ignored the careful description given by one of us of all of the products obtained by the action of sodium on acetone, the statement which she makes that "so-called sodium acetone contains 50·4 per cent of sodium" would in itself be sufficient to cause some doubt as to the accuracy of her results. In our opinion the fact that the product of the action of sodium on acetone, when all acetone and solvent have been removed, on acidifying *regenerates acetone in large amount*, is conclusive enough evidence of the existence of sodium acetone, and this fact was repeatedly emphasised in the first series of papers on this subject, but ignored by Miss Taylor in her discussion. Nevertheless, we have deemed it necessary to repeat the work, and here it may be said that at no time, even with the absence of all of the usual precautions, were we able to encounter as much as 50 per cent of sodium in the derivative of the action of sodium on acetone; in ether we obtained 29·2 to 30·9 per cent of sodium, and the highest determination (in petroleum ether) gave us 35·5 per cent, these results being in accord with those previously obtained by one of us. In carefully reading Miss Taylor's paper it becomes evident that she always had a *red* substance present after the action of sodium on acetone, both in her experiments on the determination of the amount of sodium in the insoluble precipitate and in the soluble portion. It has in the past been expressly stated that sodium-acetone, when prepared with all precautions, is *white*, and that reddening is due to decomposition in the air or by reason of moisture.

Experimental.

Sodium acetone is a very delicate substance. When properly prepared and when air and moisture are rigidly excluded it is a *snow-white*, flocculent solid. On exposure to the air and to moisture it becomes pink, then red and brown, an oil at the same time separating, the colour changes representing the formation of sodium hydroxide and condensation products of acetone. Of course, as had previously been shown, sodium acetone also contains sodium isopropylalcoholate, and some sodium pinaconate and, in the reactions performed under ether, some sodium ethylate. All ether which we used in these experiments was repeatedly dried and distilled from sodium wire until this wire would remain perfectly bright under the solvent. The acetone was from the bisulphite compound and was dried four times over phosphorus pentoxide, each time being poured off and distilled. Dry hydrogen was run through the acetone for some hours to remove any air or carbon dioxide, and it was then kept over fused sodium sulphate and protected from moisture and carbon dioxide by tubes containing phosphorus pentoxide and soda-lime.

Experiment 1.—The apparatus used was that described by Freer (*Am. Chem. Journ.*, 1893, xv., 588). About 1·6 grms. of sodium, cut under coal oil and then washed with absolute ether, were quickly squeezed as a very fine wire into about 50 cc. of absolute ether in the reaction flask, and the apparatus quickly closed. Dry and pure hydrogen was now run through the apparatus for three hours. The reaction flask was then surrounded by ice and 10 cc. of acetone, dissolved in 50 cc. of absolute ether, gradually added through a dropping funnel. Bubbles of hydrogen were given off and the separation of a white, gelatinous precipitate soon commenced. When all of the sodium had disappeared, the ether and precipitate were sucked into a filtering tube, the latter washed eight times with absolute ether, using 50 cc. each time and always sucking as dry as possible. The precipitate was then dried to constant weight in a current of hydrogen, weighed, and decomposed with dilute, ice-cold sulphuric acid. Only a minimal amount of acetone-condensation products was obtained, as the sodium salt was practically completely soluble in water. In no instance, if the sodium derivative had been properly prepared, was there more than a drop or two of insoluble oil. When small amounts of air or moisture gain access to the sodium derivative, or when the decomposition by acids is not carefully conducted, then these condensation products result, the greater the decomposition, the greater their amount.

2·65 grms. pure white sodium acetone were obtained, containing 0·8052 grm. sodium.

	Required for C_3H_5ONa.	Found.
Sodium (per cent).. ..	28·75	30·3

The acid solution resulting from the decomposition of the product of the action of sodium on acetone was now rendered alkaline with ammonia, and iodine, dissolved in ammonium iodide, added until the colour of iodine no longer disappeared. There resulted 6·5 grms. of iodoform, equal to 1 grm. acetone or 53 per cent of the amount calculated for pure sodium acetone. Undoubtedly, some loss of iodoform occurs in evaporating its ethereal solution, and all acetone is not converted into iodoform, so that the percentage of acetone is probably really higher than given above.

(Note.—We have once more tested this method of determining acetone in the presence of isopropyl or ethyl alcohol, and can substantiate the former statements of Freer that it is sufficiently accurate for the work in hand, the results being *under* rather than over the amount of acetone. Denigès' very convenient method of acetone determination is unsuitable, as both isopropyl alcohol and mesityloxide give precipitates with his reagent. Denigés, *Comptes Rendus*, 1898, cxxvii., 963; *Ann. Chim. Phys.*, 1899, [7], xviii., 400; *Bull. de la Soc. Chim.*, 1899, [3], xxi., 241. Oppenheimer, *Ber.*, 1899, xxxii., 986; *Chem. Centrbl.*, 1899, [2], 888).

Experiment 2.—About 1·5 grms. sodium wire were dissolved in an excess of acetone diluted with absolute ether, the whole being in an Erlenmeyer flask having a very small neck. The flask was not surrounded by ice, the heat generated by the reaction evidently volatilising enough ether, to exclude air, the sodium derivative remaining white. The sodium compound was now rapidly filtered on a Hirsch funnel with strong suction, quickly washed six times with ether and then dried in a vacuum desiccator over sulphuric acid and paraffin. The salt was somewhat pink, but as soon as it was dry it was weighed to a tenth of a grm. as quickly as possible and then thrown into ice-cold, dilute acid. The acid was now saturated with potassium carbonate and the low-boiling portion distilled on a water-bath. The distillate was saturated with a solution of sodium bisulphite and the whole cooled in ice for one hour. The acetone sodium-bisulphite (4·5 grms. from 3·8 grms. sodium compound) was filtered and decomposed with sodium carbonate, the acetone being distilled. There resulted 1 grm. of acetone boiling at 54° to 57.

Experiment 3.—This was carried out exactly as was Experiment 2, with the difference that a sodium determina-

tion was made by using an excess of standard acid (found 30·9 per cent). This experiment gave 4·2 grms. of iodoform, corresponding to somewhat less than one-half the theoretical yield of acetone for pure sodium acetone.

As will be seen, even in the above two experiments, when air was not rigidly excluded and where the sodium derivative was not handled with particular care, no such high percentage of sodium as that obtained by Miss Taylor was found. Indeed, in a long series of experiments we have never been able to obtain her results, which could only be accounted for by a profound decomposition of her sodium derivative and the washing out of the acetone condensation products which would be formed. If this decomposition were allowed to go far enough, then practically nothing but sodium hydroxide mixed with the sodium derivatives of alcoholic reduction products would remain.

Experiment 4.—This was performed as was Experiment 1, with the exception that petroleum ether was substituted as a solvent. The reaction in this case is not so clean cut as with ether, the resulting compound is somewhat pink, and the sodium percentage higher.

1·745 grms. of the sodium derivative gave 0·6203 grm. Na and 3·4 grms. iodoform, equivalent to 35·5 per cent sodium and 0·52 grm. acetone, 41 per cent respectively.

Experiment 5.—The apparatus was the same as in Experiment 1. 8·515 grms. of the sodium compound was obtained, giving 2·567 grms. of sodium, equivalent to 30·14 per cent. After the sodium salt had been decomposed, the acid solution was divided into four parts. One of these was saturated with sodium acetate, then made very slightly alkaline, and the theoretical quantity of semicarbazide hydrochloride was added. A precipitate of crystalline needles rapidly formed. After the mixture had stood for twelve hours in the ice-chest the precipitate was filtered, and it gave 1·2 grms. of acetone semicarbazone, melting-point 186°. This was identical in all respects with a specimen of the same body prepared for comparative purposes. One-eighth of the original acidified solution gave 1·3 grms. of iodoform.

Experiment 6.—The conditions were the same as in Experiment 1. 8·25 grms. of sodium derivative were obtained; from one-half of this, acidified, &c., 2·9 grms. acetone semicarbazone, melting at 186°, were separated, and from one-quarter, 2·2 grms. iodoform were precipitated. One other sodium determination gave us 29·2 per cent of sodium.

The above experiments render it practically certain that a sodium derivative of acetone exists among the products of the action of sodium on acetone, as acetone is obtained by their decomposition with acids. However, it might possibly be true that the reaction product is sodium isopropylate together with some caustic soda, and that the acetone which is found is held by the sodium isopropylate in a combination somewhat similar to alcohol of crystallisation. That this is unlikely is proved by the fact that the sodium derivative formed by the action of sodium on acetone, after filtering and washing, was dried *in vacuo* to constant weight, while at the same time it was *warmed* to beginning decomposition. If acetone were present in a condition such as the above, it certainly would be driven off by this treatment; nevertheless, the sodium derivative behaved as usual when it was added to dilute acid. That sodium isopropylate does not behave as does sodium acetone, even when it is mixed with acetone, is shown by the next experiment.

Experiment 7.—2·5 grms of sodium were dissolved in an excess of isopropyl alcohol, and diluted with absolute ether. The white colour did not change in the least when the derivative was allowed to stand for three hours in an open beaker, whereas the pro luct of the action of sodium on acetone, placed beside it under the same conditions, decomposed and completely changed in five minutes. When acetone was added to sodium isopropylate under ether, the resulting mixture remained unchanged for a long time when exposed to the air, although after one hour it had assumed a slightly pink tinge. It was now filtered washed three times with absolute ether, dried, and thrown into dilute sulphuric acid. The usual acetone test gave no trace of iodoform. Acetone is therefore not retained by sodium isopropylate.

Miss Taylor suggests that the reaction first observed by one of us may be due to the formation of the sodium salt of diacetone alcohol, $(CH_3)_2.COH.CH_2.CO.CH_3$. This compound is formed from acetone in the cold under the influence of hydroxyl ions. Koelichen (*Zeit. Phys. Chem.*, 1900, xxxiii., 129; Heintz, *Liebig's Ann. Chem.*, 1873, clxix., 114) has shown that in the presence of hydroxyl ions there is an equilibrium between the amounts of acetone and of diacetone alcohol; thus with a concentration of hydroxyl ions represented by a 10 per cent solution of sodium hydroxide, the quantity of diacetone alcohol is 3 per cent of the total acetone, and smaller in quantity for a lower concentration of the ions. The sodium compound of this body would contain 14·37 per cent of sodium. We have prepared diacetone alcohol according to the method of Koelichen, and subjected it to the action of sodium. The alcohol was diluted with absolute ether, and in an open beaker dissolved sodium very rapidly, with marked reddening of the resulting compound, the action resembling closely that observed when acetone is similarly treated in the open air, but on acidifying the product, mesityl oxide and other condensation products of acetone are separated, and acetone could be demonstrated in the solution by the formation of its semicarbazone, melting at 185° to 186°.

A different result is obtained in an atmosphere of dry hydrogen. In the apparatus used in Experiment 1, and under absolute ether, diacetone alcohol is only very slowly attacked by sodium, giving a yellowish sodium derivative. Over four hours were consumed in dissolving 0·5 grm. of sodium in 5·5 grms. of the alcohol. The precipitate was filtered, dried in a current of hydrogen, and dissolved in dilute acid, a considerable quantity of condensation products of acetone separating. 0·74 grm. of the sodium derivative gave 1·067 grm. sodium sulphate, or 46·8 per cent sodium. It seems evident, therefore, that sodium acting on diacetone alcohol, really does give sodium hydroxide and the condensation products of acetone; the reaction is, however, so radically different from the action of sodium on acetone, and the condensation products so prominent (there are scarcely any when pure sodium acetone is dissolved in dilute acids) that the theory that diacetone alcohol is first formed, subsequently to be acted on by sodium, must be abandoned. There remains only the question, then, of whether sodium acetone could not react with acetone to give the sodium derivative of diacetone alcohol, although in this event the percentage of sodium found should be very much less than it really is. However, apart from this, in the absence of condensation products of acetone on acidifying, it must be presumed, to account for the acetone which is always found in the acidified solutions of sodium acetone, that the diacetone alcohol would promptly be re-converted into acetone during this process. Rigidly to exclude this supposition we performed the following experiment.

To be continued)

Decahydro-α-naphthylacetone and Decahydro-α-naphthylamine.—Henri Leroux.—When α-naphthol is hydrogenated by the catalytic method with nickel, decahydro-α-naphthol is produced. When oxidised with chromic acid this yields decahydro-α-naphthylacetone, which possesses the general properties of acetones. The reduction of its oxime by sodium in presence of absolute alcohol yields decahydro-α-naphthylamine, which is a very energetic base, forming well-defined salts with acids. —*Comptes Rendus*, cxliv., No. 18.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 2nd, 1907.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Mr. A. V. Hussey was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Owen Aubrey Elias, 123, Waller Road, New Cross, S.E.; Walter Harold Nuttall, 55, Market Street, Watford, Herts; Walter Ormston Young, Springfield, Cartmel, Lancs.; Israel Hyman Zortman, B.Sc., Sternwartenstr. 44 II. r. Leipzig.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—John Campbell Allan; Francis James Bailey; William Robert Ball, B.Sc.; Kenneth Somerville Caldwell, B.Sc., Ph.D.; Alexander Thomas Cameron, M.A., B.Sc.; John Arthur Cunningham, B.A.; Thomas Kirkman Dealy; Samuel Duckworth, B.Sc.; John Jacob Fox; Charles Stanley Gibson, B.A.; Joshua Craven Gregory, B.Sc.; Joseph Henry Hall, B.Sc.; Arthur George Harrington; Thomas Featherstone Harvey; Geoffrey Doddleston Hope, B.Sc., Ph.D.; Edward Houghton; Hon. Raymond Egerton Hubbard; Herbert Brooke Perren Humphries, B.Sc.; Carl Lewis; James McConnan, M.Sc., Ph.D.; Herbert Victor Mitchell; Percy Joseph Rhodes; Frederic William Rixon, M.Sc., Ph.D.; John Robinson; Sydney William Smith, B.Sc.; George Colleymore Sturrock, Capt. R.A.; Sam Mortimer Sutcliffe; Nicholas Tarr; William Scott Tebb, M.A., M.D.; William Griffiths Tonner, B.Sc.

Of the following papers, those marked * were read:—

*90. "*The Chemical Action of the Radium Emanation.* Part I. *Action on Distilled Water.*" By Sir William Ramsay, K.C.B.

A qualitative confirmation of the fact noticed by Rutherford that the emanation from radium, in decaying, evolves a large amount of heat has been obtained; the relative amounts of hydrogen and oxygen produced by the action of radium bromide on water amounting to 32 cc. of explosive gases per grm. of radium per one hundred hours, have been measured, and also the excess of hydrogen, of which the mean value is 5·5 per cent, reckoned on the total gas. Reasons were adduced to show that hydrogen is not one of the products of degradation of radium, and other hypotheses to account for the excess of hydrogen were considered.

The action of the emanation alone on water also decomposes it into explosive gas, mixed with excess of hydrogen; it has been shown that the emanation, when mixed with explosive gas, causes re-combination, and the rate at which the decomposition of water takes place has been measured.

The reason of the production of excess of hydrogen has not yet been elucidated.

Discussion.

Prof. Tilden said that although the subject which had been brought before them by the President would probably not admit of much discussion, they would be ready to unite in expressing their admiration of the remarkable skill which had been displayed in the manipulation and measurement of such strange material in quantities so minute. They must also commend the self-restraint which Sir William Ramsay had imposed on himself in refraining from speculation in a field which offered so much temptation and where there was room for so much difference of opinion.

The President, in answer to a question, replied that the emanation was an inactive gas, in the sense of not orming compounds, but at the same time, a most active gas, inasmuch as it decomposes or disintegrates into a series of other bodies, some of which, at least, are capable of chemical combination.

*91. "*Freezing-point Curves of the Menthyl Mandelates.*" By Alexander Findlay and Evelyn Marion Hickmans.

From a study of the freezing-point curve for mixtures of *l*-menthyl *l*-mandelate and *l*-menthyl *d*-mandelate, it is found that *l*-menthyl *r*-mandelate exists as a definite, partially racemic compound having a stable melting-point of 83·7°. By applying the law of mass action and the law of the depression of the freezing-point by dissolved substances, the degree of dissociation of the partially racemic compound has been calculated to be about 50 per cent. It was also pointed out that other freezing-point curves indicate the existence of true racemates in the liquid state.

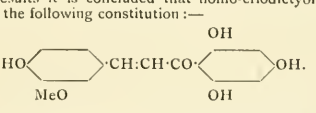
Discussion.

The President asked whether it had been proved that racemic compounds possessed double the molecular weight of the *d*- or *l*-compounds, and whether they might therefore be regarded as composed of one molecule of each variety.

Dr. Findlay, replying to Dr. Lowry, stated that calculations had not been made with regard to the stability of hydrated salts, but that the method of calculation referred to would be applicable also in such cases. In reply to the President, Dr. Findlay stated that the arguments adduced for the existence of a racemic compound held only for the fused state, not for solutions, although it is highly probable that undissociated racemic compounds exist to some extent even in solution.

*92. "*The Constitution of Homo-eriodictyol. A Crystalline Substance from Eriodictyon Leaves.*" By Frederick Belding Power and Frank Tutin.

The substance designated *homo-eriodictyol*, $C_{16}H_{14}O_6$ (m. p. 223°), previously isolated and described by the authors (*Pharm. Journ.*, 1906, lxxvii., 381, and *Abstr.*, 1906, xc., [ii.], 885), has now been further investigated. It is isomeric with hesperitin (*Ber.*, 1881, xiv., 979), and similar to the latter in many of its properties, but its sodium compound has the normal formula $C_{16}H_{13}O_6Na$ (compare Perkin, *Trans.*, 1898, lxxiii., 1037). Homo-eriodictyol contains one methoxyl group, and yields a *tetra-acetyl* derivative, $C_{16}H_{10}O_6(COMe)_4$ (m. p. 154°). On fusion with potash it gives protocatechuic acid. When homo-eriodictyol is hydrolysed with a concentrated aqueous solution of potassium hydroxide it yields phloroglucinol and ferulic acid (4-hydroxy-3-methoxycinnamic acid). From these results it is concluded that homo-eriodictyol must possess the following constitution:—



The "eriodyctionon" recently described by Mossler (*Annalen*, 1907, cccli., 233), is evidently identical with homo-eriodictyol.

Eriodictyol, $C_{15}H_{12}O_6$ (m. p. 267°), a crystalline substance which was also isolated by the authors from eriodictyon leaves (*loc. cit.*), contains no methoxyl group. When heated with acetic anhydride it yielded two compounds, melting at 137° and 195—196° respectively. It is considered probable that homo-eriodictyol is a monomethyl ether of eriodictyol.

93. "*The Relation between Valency and Heats of Combustion.*" (Preliminary Note). By Gervaise Le Bas.

It is now known that a valency is a volume property of the atoms (Barlow and Pope, *Trans.*, 1906, lxxxix., 1675; Le Bas, *Trans.*, 1907, xci., 312), and the author has found that valency may also be regarded as an energy property; this conclusion can be illustrated with the aid of the heats of combustion of the hydrocarbons.

The heat of combustion of a substance may be regarded

as made up of (*a*) an absorption of heat due to the dissociation or decomposition, and (*b*) an evolution of heat due to the combination of the isolated atoms with oxygen. A study of molecular heats of combustion, however, reveals the following law, which appears to be generally valid:—*The heat of combustion of an organic compound is equal to the sum of the heats of combustion of its possible dissociation products.*

The conclusion is therefore drawn that the factor *a* is negligibly small as compared with *b*. In illustration of this may be cited the facts that the heats of combustion of a normal paraffin and its carboxyl derivatives are identical provided that the physical state be taken into account, and that the heats of combustion of associated substances or of polymerides are the same as those of an equivalent number of simple molecules. It may be shown that the thermal constants of the alcohols, ethers, organic halogen compounds, carboxylic acids, esters, nitriles, amines, mercaptans, and other classes of compounds also follow this law.

The heats of combustion of organic compounds in most cases are found to be the same as those of saturated and unsaturated hydrocarbons and hydrogen, or of mixtures of these. Similarly, the factor *a* is negligibly small as compared with *b* in the case of the saturated and unsaturated hydrocarbons, and therefore their heats of combustion are sensibly those of their isolated atoms, *plus* an excess for the latter, owing to unsaturation. The additive relations obtained lead to a second law which applies to all the hydrocarbons.

The molecular heats of combustion of the hydrocarbons are proportional to their valency numbers W. For example, the heat of combustion of a normal paraffin, C_nH_{2n+2}, in the gaseous state is given by the expression $M.H.C. = (6n+2)c = W.c.$, c being a constant, representing the heat equivalent of one hydrogen atom expressed in large calories.

This law is illustrated by the following table, in which Thomsen's values are used:—

	W.	*c.*	W.*c.*	Calc. M.H.C.
Methane, CH_4 ..	8	26·49	211·7	211·9
Ethane, C_2H_6 ..	14	26·45	370·4	370·4
Propane, C_3H_8 ..	20	26·46	529·2	529·2
Butane, C_4H_{10} ..	26	26·43	687·9	687·2
Pentane, C_5H_{10} ..	32	26·46	846·7	847·0
Mean..		26·46		

The heat value of the difference for the homologous increment CH_2 is calculated to be equal to $6c = 6 \times 26{\cdot}46 = 158{\cdot}76$, which is similar to that observed.

The conclusion is also drawn that the molecular heats of combustion of compounds do not lend themselves to the determination of constitution. From certain peculiarities which are connected with olefine and acetylene linkings, it is, however, possible to recognise the presence of the latter in a compound with certainty.

94. "*The Velocity of Hydrolysis of Aliphatic Amides by Alkali.*" By JAMES CODRINGTON CROCKER and FRANK HAROLD LOWE.

The rate of reaction of the aliphatic amides with sodium hydroxide has been investigated at from 40·06° to 95·9°.

The reactions are shown to follow the bimolecular relation—

$$K = \frac{1}{at}\left[\frac{1}{c} - \frac{1}{c^0}\right],$$

where a is the degree of dissociation of the alkali. The graphs between the reciprocal of concentration and time are very approximately straight lines with a slight curvature indicating a small retarding effect of the neutral salt. If the amides are arranged in decreasing order of reactivity, this order is:—Formamide, acetamide, propionamide, capronamide, butyramide, *iso*butyramide, valeramide; the temperature variation of reactivity over the above range is best expressed by the formula—

$$\log K = \log K^0 + B\left(\frac{1}{T^0} - \frac{1}{T}\right) + C\left(\frac{1}{T^0} - \frac{1}{T}\right)^2.$$

The mean differential coefficient of the graph between $\log K$ and $\frac{1}{T}$ for the above range is less than for the analogous case of hydrolysis by acid. The view is taken that hydrolysis by alkali of the amides proceeds by the direct action of the hydroxyl ion on the amide molecule. A modification of the Arrhenius hypothesis was suggested to explain the exponential variation of reactivity with temperature, a parallel being drawn between tautomeric change, where difference of property is produced by the "wandering" of an atom, and "electromeric" change, where difference of property is caused by the movement of an electron.

95. "*The Addition of Iodine to Acetylenic Acids.*" By THOMAS CAMPBELL JAMES and JOHN JOSEPH SUDBOROUGH.

Good yields of the di-iodides of tetrolic and phenylpropiolic acids are formed when a concentrated aqueous solution of cupric sulphate (1 mol.) is gradually run into a well-stirred aqueous solution of the potassium salt of the acid (1 mol.) mixed with an excess of potassium iodide. The di-iodides may be isolated by warming the solution, removing the cuprous iodide, and acidifying with a mineral acid.

The same di-iodides may be prepared by mixing aqueous solutions of the potassium salts with an excess of a potassium solution of iodine in iodide and allowing to stand for several days.

Definite di-iodides could not be isolated from *o*- and *p*-nitrophenylpropiolic acids, or from acetylenedicarboxylic acid, although in the two former cases an addition of iodine occurs.

Olefinic acids, even when they contain conjugated bonds, do not combine with iodine to any appreciable extent.

The velocity constants for the reactions between a solution of iodine in potassium iodide and the potassium salts of tetrolic, phenylpropiolic, *o*- and *p*-nitrophenylpropiolic acids have been determined. The reaction in each case is bimolecular when aqueous solutions are employed.

The reaction between iodine and phenylpropiolic acid has been studied in absolute alcohol and in aqueous alcoholic solutions, both with and without the addition of potassium iodide.

96. "*The Chemical Changes Induced in Gases submitted to the Action of Ultra-violet Light.*" By DAVID LEONARD CHAPMAN, SAMUEL CHADWICK, and JOHN EDWIN RAMSBOTTOM.

An apparatus specially designed for the examination of the chemical changes brought about in gases by the influence of the light emitted from a mercury lamp was described. With the aid of the apparatus the conversion of oxygen into ozone, the interaction of carbon monoxide and oxygen, and the decomposition of carbon dioxide have been investigated particularly with a view to ascertaining the effect, in each case, of the presence of varying amounts of water-vapour.

Dry carbon dioxide is decomposed by ultra-violet light, the percentage decomposition being increased by a reduction of pressure, but, under the same conditions, the moist gas at all pressures remains practically unchanged. The rate of contraction of a mixture of carbon monoxide and oxygen is practically independent of the degree of desiccation of the gases, and this was found to be due to the fact that, although the presence of moisture causes the rate of formation of carbon dioxide to rise, it results in an equivalent reduction in the yield of ozone.

97. "*Studies of the Perhalogen Salts.*" (Part I.). By CHARLES KENNETH TINKLER.

The well known formation of periodides by the addition

of iodine to a solution of an iodide has been investigated by means of the ultra-violet absorption spectra of the solutions. Whilst neither a N/100 aqueous solution of iodine nor dilute solutions of iodides show any characteristic absorption in the ultra-violet, the aqueous solutions of iodine, after the addition of various iodides, all give the same spectra, which show a large amount of general absorption and two absorption bands.

Solutions of iodine to which various soluble bromides or chlorides have been added also give evidence, from their spectra, of the presence of addition compounds of the halogen salt and iodine.

It can be shown from the spectra of the solutions, that with equimolecular quantities of potassium iodide, bromide, or chloride, combination take place most readily with the iodide, and least with the chloride. On the addition of hydriodic, hydrobromic, or hydrochloric acids to the aqueous solution of iodine, the spectra of the solutions are the same as those containing the corresponding metallic salts; hydriodic acid, however, appears to combine with iodine when the acids are passed into a chloroform solution of this substance.

98. "*The Interaction of Cyanodihydrocarvone, Amyl Nitrite, and Sodium Ethoxide.*" By Arthur Lapworth and Elkan Wechsler.

Cyanodihydrocarvone, when subjected to the action of amyl nitrite and sodium ethoxide, is converted into a compound, isomeric with the expected *iso*nitroso-derivative, but which investigation has shown to be a *lactam*, $C_{10}H_{14}ON\langle^{NH}_{C}$; this is feebly acidic, and may be converted into a neutral *methyl* derivative, $C_{10}H_{14}ON\langle^{NMe}_{CO}$.

On treatment with dilute alkali these yield the corresponding *amino-acids*, from which they may again be obtained by means of dehydrating agents.

The lactams are converted by cold acids into *lactonic bascs*,—

$C_{10}H_{15}ON\langle^{NH_2}_{CO}\!\!-\!\!O$ and $C_{10}H_{15}ON\langle^{NHMe}_{CO}\!\!-\!\!O$

which, on hydrolysis with hot dilute acids, yield ammonia and methyl amine respectively, together with a *lactonic acid*,—

$C_{10}H_{17}O_2N\langle^{OH}_{CO}{}'\!\!-\!\!C$

which, although it may be titrated in the cold as a monobasic acid, is probably not carboxylic in character; with warm alkalis the lactone ring is severed and the compound behaves as a dibasic acid.

All these compounds, by prolonged treatment with hot mineral acid, are converted into a pseudo*cumene carboxylic acid*, ($CO_2H : Me_3$ = probably 1:2:3:5). This is dimorphous, the forms melting at 84° and 105—106° respectively.

99. "*Contributions on the Chemistry of Oxygen Compounds. II. The Compounds of Cineol, Diphenyloxide, Nitroso-derivatives, and the Carbamides with Acids and Salts.*" By Robert Howson Pickard and Joseph Kenyon.

The authors have investigated the capacity of various compounds containing oxygen to form additive compounds analogous to those of the phosphine oxides (Part I., *Proc.*, 1906, xxii., 42) with the view of throwing some light on the influence (if any) of the phosphorus atom. No regularity can be observed in the molecular proportion of substances containing oxygen in their additive compounds.

It is suggested that the formation of additive compounds by sulphoxides and nitroso-compounds and the non-formation of the same, in general, by sulphones, nitro- and azoxy-compounds is probably due to the position of the oxygen atoms of the latter in a ring, so that any subsidiary or residual valency is internally satisfied. As the aryl substituted carbamides form salts, and as, in general, the carbamides behave in regard to the formation of additive compounds in a similar manner to the phosphine oxides, cineol, &c., it is probable that the additive compounds formed by the carbamides are due to the subsidiary valency of the oxygen atom, which in these compounds, as in the phosphine oxides, is influenced by the proximity of the nitrogen or phosphorus atom respectively. The additive compounds of cineol with magnesium alkyl halides are decomposed when heated, and the product when treated with dilute acid yields Δ^1-*p*-terpineol (8).

Research Fund.

A meeting of the Research Fund Committee will be held in June. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before Saturday, June 8th, 1907. Those Fellows who received grants in June, 1906, or whose grants, allotted in June of previous years, have not been closed, are reminded that reports must be in the hands of the Hon. Secretaries not later than Saturday, June 1st.

Erratum.—P. 236, col. 2, line 16 from bottom, *for* "Toluoyl" *read* "Phenylacetyl."

PHYSICAL SOCIETY.

Ordinary Meeting, May 10th, 1907.

Prof. J. Perry, F.R.S., President, in the Chair.

A paper entitled "*Stereoscopy with Long Base-line, Illustrated on the Screen*" was read by Dr. T. C. Porter.

The present paper containing suggestions and extensions of stereoscopic work is largely the same as that read to the Royal Photographic Society on January 29th of the present year. The use of a long base-line for tele-stereoscopy had occurred to M. Selb, of Brussels, and in 1903 he obtained stereoscopic mountain photographs. The applications of the method for military, geographical, and meteorological purposes, although obvious, do not seem to have been used before, and the author discusses the possibilities of these applications. The paper opens with a brief sketch of the principles of stereoscopy, and describes an attempt to measure the limit of stereoscopic vision for the unassisted eye. The power we possess of judging of the difference in distance of two objects in our field of view depends, first, upon various properties of those objects which vary with the said distance, variations to appreciate which we require strictly but one eye, though it may well be that we appreciate them better with two. These properties are the apparent size, the clearness or haziness of an object, the arrangement of light and shade, and the shadows cast, and fourth, the apparent motion of the object. The next means of telling the different distances of objects depends —not on the properties of the objects themselves—but on one of the eye itself. It is the effort, made quite instinctively, by which we bring the images of objects to a sharp focus on the retina, *i.e.*, by the effort made in so-called accommodation. The power of accommodation is, however, comparatively limited in its scope, the author's experiments putting the limit for ordinary sight at about six feet from the eye. On these various methods and on the mental deductions following from them and founded on previous experience, depend the whole of the powers of appreciating form and distance, so far as each eye is considered separately. The impressions received by the two eyes when regarding any near object are not the same,

because each eye sees from its own position, which differs from that of the other eye by about 2·5 inches in most cases. When an observer wishes to examine a near object he must turn each eye inwards by a certain angle θ, and this he does by making a definite effort. It is this effort of convergence which gives the sensation of spectroscopic relief. When the object is so far removed from the eye that the angle θ, or the convergence for one eye, becomes too small to be appreciated, and therefore also the effort necessary for the convergence through this small angle becomes inappreciable, the stereoscopic sensation fails. In other words, stereoscopic sensation will be limited to objects nearer the observer than this distance, which is thus the spectroscopic limit. The author's experiments place this distance for average persons at about 43 feet. The range of stereoscopic effect varies directly as the length of the base-line. If the distance between the eyes could be increased ten times, the stereoscopic effect would be perceptible to a distance of 430 feet. Such an increase of base-line can be made to all intents and purposes by means of reflectors, and this was first done by Helmholtz. The base-line can also be increased by taking two photographs of distant objects from two different points and viewing them in a stereoscope. However long the base-line, so long as its two ends are about the same distance from the objects, and so long as the objects themselves are clear enough and large enough to yield a picture, we have the means of determining the forms and relative distances of the objects however far off they may be. The author showed upon the screen numerous stereoscopic pictures of distant objects, mountains, clouds, &c., and discussed the value of the pictures for military, geographical, and meteorological investigations.

Mr. J. Tennant expressed his interest in the paper, and said he had shown pictures of clouds, taken by the same method as that employed by the author, in a paper published in 1897. He was not certain that the feeling of convergence was the only thing which determined stereoscopic vision. The estimate of 43 feet as the limit of stereoscopic vision seemed to him too small, as he had observed stereoscopic effects at distances up to 125 yards. In 1896 he devised a stereoscopic camera, and used it to measure the heights and depths of clouds. In some of his cloud experiments he had used a base-line three-quarters of a mile long. The method was applicable to many subjects, and was a most valuable one.

Mr. Crawley said the author's determination of the angle θ was very much larger than that given by Helmholtz. The methods described by the author had been used by Pulfrich in surveying and astronomical work.

NOTICES OF BOOKS.

The Value of Pure Water. By George C. Whipple. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

This book appeared originally as a collection of scientific papers, entitled "Biological Studies by the Pupils of William Thompson Sedgwick," which attracted a considerable amount of attention. The author was therefore induced to revise and publish them in book form, adding to them some extracts from lectures on aspects of the water supply question delivered at the Brooklyn Polytechnic Institute and elsewhere. The main idea is the comparison of different waters upon a financial basis, and it is very ingeniously worked out. Provisional formulæ are suggested which express approximately the depreciation due to sanitary qualities, physical characteristics, hardness, and temperature. The results obtained are then tabulated and represented graphically, and they give some idea of how to compute the value of pure water in terms of money, and should assist public authorities in deciding whether they would be justified in incurring the cost of filtration and purification. In some cases the formulæ necessarily rest more upon estimates than upon statistics, and will undoubtedly be modified in time, but the author's suggestions are of real practical value, and are worth the attention of those who are interested in the question of providing as pure water as possible for the use of the public.

Electro-chemistry. By Dr. Heinrich Danneel. Translated by Edmund S. Merriam, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

Although the treatment of theoretical electro-chemistry in this book is slight, it is sufficient to give those who are quite unacquainted with the subject a useful idea of its elements, and thus it may serve as an introduction, accurate as far as it goes, to the study of larger works. In later volumes Dr. Danneel hopes to discuss experimental electro-chemistry and its applications. The practical importance of electro-chemistry in the manufacture of various substances, otherwise difficult or expensive to prepare, and in the storing and transporting of energy, is growing so rapidly that all students of science should have at any rate an elementary knowledge of it, and those who are not going to specialise in the subject will find the book sufficiently full for their requirements. In this volume chemical statics and dynamics are discussed very briefly, and a clear exposition is given of the theory of electrolytic dissociation. The translation has been carefully performed, and the book will be found to give a clear account of the outlines of electro-chemistry.

Uber die Elektrolytische Gewinnung von Brom und Iod. ("The Electrolytic Preparation of Bromine and Iodine"). By Dr.-Ing. Max Schlötter. Halle-a.S.: Wilhelm Knapp. 1907.

The greater part of this book is devoted to the preparation of bromine, the methods of extracting iodine electrolytically being of much less interest and importance. Like the other volumes of the series of Monographs on Applied Electro-Chemistry, the book is characterised by the great thoroughness with which the subject is treated, and the fulness of the references to original papers which make them of considerable value as works of reference. The chemical methods of preparing bromine are treated shortly, while all the successful processes in which electrolysis is employed are described in detail. Information relating to yield is given, and the purification of bromine and its analysis are the subjects of two chapters. The preparation of iodine naturally requires very much less space, the electrolytic method having as yet been but little investigated, though there are indications that it will shortly be the subject of additional exhaustive research.

Essais de Jean Rey ("Essays of Jean Rey"). Edited by Maurice Petit. Paris: A. Hermann. 1907.

The name of Jean Rey is but little known to students of the history of chemistry, and the exact part he played in the furtherance of chemical knowledge perhaps even less; his fundamental work has been most unjustly overlooked, and this reprint of his lectures will therefore be all the more acceptable. If the reader will take the trouble to conquer the old French in which they are written, and which will present but little difficulty, he will find that the book is really the earliest treatise on physics, and, moreover, one which contained the account of a discovery of great importance. Jean Rey, with unique acumen to aid him in his speculations, and steady patience in collecting material, was the first of the philosophers of the Seventeenth Century to suggest and prove that the air has weight, and

that the increase of weight of the metals tin and lead upon calcination comes from the air, and is not due to vapours of carbon, soot, "volatile mercurial salt," or, in fact, any of the causes to which the ingenuity of his predecessors had ascribed it. The essays show Rey to have been an acute reasoner and close observer, and deserve to rank among the classic masterpieces of chemistry. In this edition the editor contributes explanatory notes, while the comments of Gobet, who brought out an edition in 1777, are also included. The text follows closely that of the original, which was published in 1630.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 17, April 29, 1907.

Direct Hydrogenation of Allyl Compounds.—Paul Sabatier.—The ordinary methods of hydrogenating allyl alcohol in the wet way do not readily transform it into propyl alcohol. Thus, sodium amalgam and water, and zinc in presence of hydrochloric acid, have no effect upon it, while Linnemann found that zinc and dilute sulphuric acid, after standing twenty-five hours at the ordinary temperature, convert one-third of the alcohol into propyl alcohol. The hydrogenation is, however, effected quite easily by blowing the vapour of allyl alcohol by means of hydrogen upon reduced nickel at a temperature between 130° and 170°. Almost pure propyl alcohol is thus obtained. Reduced copper at temperatures above 180° can also be used, but the reaction proceeds far more slowly, and the product contains traces of allyl aldehyde. By the same method, allyl oxide can be completely transformed into propyl oxide.

Temperature of Formation of Carbides of Strontium and Barium.—Morel Kahn.—The author placed a mixture of the oxide of one of these metals and carbon in a graphite crucible covered by a lid of the same material and fitting into a closed crucible of quicklime. The space between the two walls was filled with sugar carbon. It was found that in these circumstances the graphite crucible is hardly attacked at all. Platinum was fused in this crucible in ten minutes at the most in the electric furnace. In the case of strontium 10·3 grms. of the oxide were mixed with 3·6 grms. of carbon, *i.e.*, the theoretical quantity, and 5 or 6 grms. of this mixture were heated for twenty minutes to a temperature at least as high as the melting-point of platinum (1775°). All the oxide was then converted into carbide. With barium oxide the same result was obtained, and thus the oxides of strontium and barium are reduced by carbon at temperatures in the neighbourhood of the melting-point of platinum.

Preparation and Properties of a New Variety of Chromium.—Binet du Jassonneix.—When chromium boride, containing 10 to 15 per cent of boron, is heated in the electric furnace in crucibles of magnesium oxide in presence of a great excess of copper, and kept for three or four minutes at the boiling-point of this metal, dissociation occurs; the boron is volatilised and the chromium dissolves in the copper and separates out on cooling in a very finely divided state. To prepare more of this modification of chromium, the carbide (containing 5 to 7 per cent of carbon) and the metal (containing 0·7 per cent of silicon and 1·2 per cent of aluminium) were treated similarly. The results obtained were identical. The chromium thus prepared, which may be separated from the copper by dissolving the latter in nitric acid, forms a mass of filaments and little crystals. Its density at 17° is 7. It possesses the chemical properties of pure chromium, but is distinguished from it by the readiness with which it reacts. It does not oxidise in the air, but burns in contact with a flame. Thus, at a high temperature copper dissolves about 1·6 per cent of chromium, and the latter separates out on cooling in a very finely-divided state.

Limit of the Action of Silicon upon Copper.—Em. Vigouroux.—When copper, lead, and silicon in excess are placed in a porcelain boat and heated in a current of hydrogen, it is found that the proportion of combined silicon to copper is roughly 10 : 100, which corresponds to the compound Cu_4Si. When either bismuth or aluminium is substituted for lead, practically the same results are obtained. The silicide is not evenly distributed in each of the three metals. With lead and bismuth the greater part of it floats upon the surface, while with antimony it is distributed uniformly throughout the metal. In all cases the compound Cu_4Si is formed.

Higher Oxides of Rubidium.—E. Rengade.—The author has studied the direct oxidation of rubidium, using his apparatus in which a given weight of metal in an aluminium boat is subjected to the action of known volumes of pure oxygen. The gas is introduced gradually into the apparatus, so that too great an evolution of heat is avoided. When a sufficient volume has been absorbed the aluminium boat is heated till its contents fuse and a homogeneous product is obtained. When the quantity of oxygen corresponds to that required for the formation of the oxide, Rb_2O_2, a yellowish white mass is produced, which fuses at about 600° to a brown liquid, and solidifies on cooling to a mass of needles. If the quantity of oxygen is increased the mass remains dark brown after solidification, and with a rather greater proportion of oxygen becomes quite black, and then does not alter in colour till the maximum of oxidation, corresponding to the peroxide, Rb_2O_4, is reached. The peroxide is yellow when it has been kept for some time in the fused state and cooled in an atmosphere of oxygen at ordinary pressure. When fused *in vacuo* it remains brownish black after cooling, because it dissociates very easily, giving up oxygen *in vacuo* at 500°. If it is kept at 550°, and the oxygen is removed as it is liberated, the black oxide is obtained. Its formula is Rb_2O_3. This trioxide may be prepared more easily by allowing the theoretical amount of oxygen to act upon rubidium and heating to the melting-point. The density of the black mass is 3·53, which differs considerably from the mean of the densities of the dioxide and peroxide, and its melting-point is below 500°, while the other oxides fuse at temperatures above 600°.

Isomeric Di-oximido-succinic Acids.—A. Wahl.—When the nitrate or chlorhydrate of hydroxylamine is allowed to act upon sodium di-oxytartrate, a mixture of nitroso-cyanacetic acid and *ββ*-di-oximido-succinic acid is obtained. If the ethereal solution obtained by repeatedly extracting the product of the reaction with ether is evaporated, a thick liquid is produced, from which a yellowish crystalline mass separates. By a long series of fractional crystallisations of this with a mixture of anhydrous ether and benzene the following products can be obtained:— (1) Oxalic acid; (2) isonitrosocyanacetic acid; (3) crystals of the composition $C_4H_4N_2O_6 + \frac{1}{2}C_6H_6$. These lose their benzene of crystallisation at 190° and then have the exact composition of di-oximido-succinic acid, $C_4H_4N_2O_6$. This acid is soluble in water, alcohol, and ether; it melts at 168° to 170°, undergoing decomposition. The aqueous solution of the crystals gives with copper acetate a voluminous green precipitate, transformed on heating into blue-green crystals. These properties distinguish the acid from Söderbaum's two isomers, which both melt at 145° and 150°, and of which one, the *ββ*-acid, gives a green precipitate turning brown with acetate of copper. If a current of dry hydrochloric acid gas is passed into a solution of ethyl di-oximido-succinate (melting-point 196°) in anhydrous ether, and the solution is evaporated

in vacuo in presence of caustic potash, a white crystalline residue is left. This is the isomeric ethyl di-oximido-succinate, which differs from the first in its melting-point (143°), solubility in water, and reaction with silver nitrate.

Dibromides of Phenol Allyl Ethers. Formation of Cyclopropanols.—Tiffeneau and Daufresne.—When the dibromides of phenol allyl ethers are heated with alcoholic potassium acetate aceto-bromhydrines are formed.

$$Ar{-}CH_2{-}CHBr{-}CH_2Br \rightarrow Ar{-}CH_2{-}CH(O{-}CO{-}CH_3){-}CH_2Br.$$

These latter substances are converted into cyclopropanols when heated with alcoholic potash:—

$$Ar{-}CH_2{-}CH(O{-}CO{\cdot}CH_3){-}CH_2Br \rightarrow Ar{\cdot}CH\begin{matrix}{-}CHOH\\ \backslash CH_2/\end{matrix}$$

The cyclopropanols are distinguished by their high densities, while the isomeric oxides of ethylene, $Ar{-}CH\begin{matrix}{-}CH{-}CH_2\\ \backslash O/\end{matrix}$, have low densities. Moreover, the former are transformed into arylacetones, $Ar{-}CH_2{-}CO{-}CH_3$, and the latter into hydrocinnamic aldehydes, $Ar{-}CH_2{-}CH_2{-}CHO$.

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Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 7, 1907.

Conversion of Magnesium Organic Compounds into Amino Complexes, and their Thermo-chemical Investigation.—W. Tschelinzeff.—The author's experiments show that the magnesium organic compounds are capable of forming complexes with tertiary amines, which are completely analogous to the mono-etherates, and more or less heat is simultaneously evolved. No compounds analogous to the di-etherates are formed under ordinary conditions. As regards the influence of the radical upon the thermic effect of the union with the tertiary amines, and hence also upon the nature of the nitrogen atom, it is found that as the mass of the radical increases in the fatty series the nature of the nitrogen atom alters in such a way that the thermic effect of the action upon the amine slowly falls; when aromatic amines are used the strongly negative influence of the aromatic radical leads to a fall in the thermic effect. It is found that more heat is evolved when ammonium compounds are formed than on the formation of the oxonium salt.

Determination of Aluminium in Silicates.—F. Willy Hinrichsen.—When aluminium oxide is precipitated with ammonia, hydrofluoric and sulphuric acids, the values obtained are always lower than when potassium-sodium carbonate is used, the loss in some cases amounting to about 30 per cent of the total. To explain this it was conjectured that possibly some of the aluminium was converted by the hydrofluoric acid into fluoride, and then volatilised, although as the temperature was low no very great loss could be caused thus. It was actually found that when freshly precipitated aluminium hydroxide is treated with hydrofluoric acid, evaporated, and ignited in a covered crucible, somewhat lower values are obtained than those which correspond to the aluminium oxide used. The difference is, however, only small, and there must therefore be some other source of error in precipitating aluminium oxide with ammonia, and adding hydrofluoric and sulphuric acids. It was then found that the last traces of hydrofluoric acid are retained by sulphuric acid in presence of alumina. Possibly some ammonium fluoride is formed, which then reacts on the hydroxide as follows:— $Al(OH)_3 + 3NH_4F = AlF_3 + 3NH_4OH$. When a solution of aluminium sulphate is acidified with hydrofluoric acid, ammonia is added, and the whole cooled, a crystalline precipitate of the double salt, $(NH_4)_3AlF_6$, separates out. Thus the difference between the found and calculated values is due to the fact that the salt was not completely freed from a small amount of ammonium fluoride, and the amount of fluorine retained depends upon whether the vessel is heated evenly on all sides or only from beneath. In this method of determining aluminium the sulphuric acid must be completely evaporated, and the residue ignited at a low temperature in order to expel all the fluorine.

Cerium Sesquioxide.—Alfred Burger.—The reduction of cerium dioxide by means of metallic calcium does not yield the metal, but a substance which on analysis is found to be the sesquioxide. The author's experiments with calcium led to the formation of a light yellowish green powder. This was treated with ammonium chloride solution, and cooled to −10°. After it had stood for an hour the oxide was rapidly separated off, washed with ice-water, alcohol, and ether, and dried *in vacuo* over sulphuric acid. When heated it yields the dioxide at about 200°. Also when kept in closed vessels it takes up oxygen comparatively easily.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, May 28, at 3 o'clock, Prof. G. H. F. Nuttall delivers the first of two lectures at the Royal Institution on "Malaria, Sleeping Sickness, Tick Fever, and Allied Diseases," and on Saturday, June 1, Sir William White begins a course of two lectures on "The Contest between Guns and Armour." The Friday Evening Discourse on June 7 will be delivered by Prof. Sir James Dewar, on "Studies in High Vacua and Helium at Low Temperatures."

MEETINGS FOR THE WEEK.

TUESDAY, 28th.—Royal Institution 3. "Malaria, Sleeping Sickness, Tick Fever, and Allied Diseases," by Prof. G. H. F. Nuttall, F.R.S., &c.
— Society of Arts, 8. "Sheffield Plate and Electro-plate," by Sherard Cowper-Coles.
— Faraday Society, 7.50. Annual General Meeting. "Contributions to the Chemistry of Gold," by F. H. Campbell. "Reduction of Oxides, Sulphides, &c., by means of Metallic Calcium," by F. M. Perkin. Exhibition of Thermostatic Apparatus, by T. M. Lowry.

THURSDAY, 30th.—Royal Institution, 3. "Chemical Progress—Work of Berthelot, Mendeleeff, and Moissan," by Prof. Sir James Dewar, F.R.S., &c.
— Society of Arts, 4.30. "Irrigation Colonies in India," by Laurence Robertson, I.C.S.

FRIDAY, 31st.—Royal Institution, 9. "Recent Journey Across Africa," by A. Henry Savage Landor.

SATURDAY, June 1st.—Royal Institution, 3. "The Contest between Guns and Armour," by Sir William H. White, K.C.B., F.R.S., &c.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2479.

THE VOLUMETRIC ESTIMATION OF FREE ACID IN PRESENCE OF COPPER AND OTHER METALLIC SALTS.

By W. EDGAR SIMS, M.Sc. (Vict.).

The various methods which have been proposed for the estimation of free acid in solutions of metallic sulphates, and especially in copper solutions, such as galvano-plastic bath liquors, are either tedious and complicated or wanting in accuracy, owing to the difficulty of obtaining an indicator giving a sharp and definite end-reaction on neutralisation of the free acid.

Sutton in his book on Volumetric Analysis recommends the use of a standard ammoniacal copper solution, which, though giving reliable results, must be frequently re-standardised on account of its liability to alter in strength. For the estimation of free sulphuric acid in copper sulphate solutions F. Hoffmann (*Chem. Zeitung*, xvii., 1318) devised the following method :—A small quantity of copper solution, containing about 2 to 3 grms. $CuSO_4.5H_2O$, is precipitated by a slight excess of potassium ferrocyanide, made up to a certain volume, and allowed to settle. The clear solution is filtered from the precipitate of ferrocyanide of copper, and titrated with standard caustic alkali. The author also states that the effect of small quantities of proto-salts, on the results, is very slight, and may for technical purposes be overlooked.

Woginz and Kittel (*Chem. Zeitung*, xxx., 1300) recommend direct titration of the free acid in galvano-plastic baths, with standard caustic alkali, using Congo-red paper as an indicator. R. T. Thomson in his excellent paper on Indicators pointed out that the sulphates of copper, zinc, and iron are neutral to methyl-orange, and R. M. Caven (*Journ. Soc. Chem. Industry*, 1900, xviii.) in his work on "The Reaction of Magnesium, Zinc, and Iron with Solutions of Copper Sulphate," adopted this indicator for the estimation of free acid in solutions of the sulphates of the above metals. The method adopted was as follows :—A blank solution was prepared containing the same amount of the sulphates of copper, zinc, or iron as the solution to be tested. Equal quantities of the solution of methyl-orange were added to the two liquids, and the purple solution containing the free acid titrated with N/10 caustic alkali, until its colour matched the pure green of the blank solution. All of these methods are more or less wanting in sharpness of the end reaction, and the use of caustic alkali is objectionable on account of its tendency to precipitate the metallic hydrates during momentary local alkalinity, which also mask the end reaction besides reducing the accuracy of the test. After many experiments a method was devised free from these objections, in which the solution remains absolutely clear during the titration, even when the alkali is in slight excess ; the utility of the test is greatly increased thereby, as it is capable of being carried out by an intelligent workman.

The method is dependent upon the following conditions :—1. The bicarbonates of these metals are slightly but sufficiently soluble for the purpose of keeping the solution clear, and are neutral to methyl-orange, whereas bicarbonate of soda is strongly alkaline to the same indicator. 2. The red colour of an acid solution of methyl-orange and the blue colour of a sulphate of copper solution are complementary, and when mixed in the proper proportions give an almost colourless solution. For example, if to 100 cc. of a 3 per cent solution of pure copper sulphate four drops of a methyl-orange solution be added, a pure yellowish green colour is produced. If to this green solution a N/2 solution of sulphuric acid be carefully added, it will be noticed that after the addition of two drops or 0·1 cc. the solution becomes practically colourless. At this stage the further addition of one drop of N/2 acid produces a distinct pink coloration, whilst the addition of one drop of N/2 bicarbonate of soda produces a distinct green coloration, the original green of the neutral solution only being obtained after the addition of two drops or 0·1 cc. of the N/2 bicarbonate. The further addition of bicarbonate produces no marked change in colour, and no precipitate until a considerable excess has been added.

The colourless stage of the solution and the remarkably sharp change to pink or green according to whether an excess of acid or alkali is added, gives an excellent indicator in the titration of the free acid in solutions of sulphate of copper, even when containing large proportions of the sulphates of nickel, iron, zinc, &c.

The titration is carried out in the following manner :—Three grms. of the sulphate of copper crystals or such a quantity of the solution to be tested as would contain about that weight of sulphate of copper, is put into a 10 oz. conical flask, and diluted with 100 cc. of distilled water, then add four drops of methyl-orange solution. If the colour produced is pink, the solution is titrated with N/2 bicarbonate of soda until the colourless stage is reached ; the amount of free acid in the material tested is equivalent to the number of cc. of N/2 carbonate used, plus 0·1 cc. If, however, the colour produced on the addition of the methyl-orange is green, then the acidity of the solution cannot be greater than the equivalent of 0·1 cc. N/2 bicarbonate, and in this case the solution is titrated to the colourless stage with N/2 acid ; the amount of free acid in the solution is therefore equivalent to 0·1 cc. minus the number of cc. of N/2 acid used.

The determination of the free acid in solutions of sulphate of copper by this method is accurate to 0·04 per cent of free acid on the weight of sulphate employed, but involves a constant correction of 0·08 per cent or 0·00245 grm. H_2SO_4 above the actual amount shown by titration with N/2 bicarbonate to the colourless stage.

The end reaction is still sharp in 5 per cent solutions, and if preferred N/10 solutions of acid and bicarbonate may be employed, but for all practical purposes the above strengths will be found most suitable for works or laboratory use.

The method is also applicable to salts of nickel or iron, &c. ; such, for example, as galvaniser's "pickle," in which case stronger solutions may be employed than with coloured salts, such as sulphate of copper or nickel.

A VOLUMETRIC METHOD OF ESTIMATING MERCURY.

By P. W. ROBERTSON.

Double mercuric sulphocyanides of the type $XHg(CNS)_4$, where X is a divalent metal, such as zinc, cadmium, or copper, were prepared by Clève some fifty years ago (*Journ. Prakt. Chem.*, xci., 227). Since that time other similar compounds have been obtained, and it has become generally recognised that the grouping $Hg(CNS)_4$ acts as a complex ion. Clève described the zinc salt, $ZnHg(CNS)_4$, as a slightly soluble crystalline substance. The composition of this compound was confirmed by the following three methods :—

(*a*) Direct determination of the mercury by distillation with lime of a sample dried at 100°. Hg = 39·9 per cent, calculated for $ZnHg(CNS)_4$ = 40·2 per cent.

(*b*) Synthesis of the salt from a known weight of mercury.

Mercuric oxide was dissolved in dilute nitric acid, and enough ammonium sulphocyanide was added to dissolve the precipitate of mercuric sulphocyanide first formed. To

this solution was then added excess of zinc sulphate, and the precipitate was collected on a Gooch crucible, and dried at 100°. Hg = 40·0 per cent, calculated 40·2 per cent.

(*c*) The amount of sulphocyanide required to precipitate a definite quantity of a solution of mercuric nitrate in dilute nitric acid was found by titrating the excess with standard silver nitrate. Numerous determinations at different dilutions and with varying excesses of zinc sulphate and sulphocyanide yielded results in accordance with the above formula.

A determination of the solubility of zinc mercuric sulphocyanide at 15° showed that 1000 grms. of water dissolved 2·4 grms. of the salt. In the presence of excess of zinc ions the solubility is considerably reduced, so that if an excess of a zinc salt is employed and the precipitate is washed with a solution of this salt, it is evident that the insolubility of this double compound can be employed to serve as a method of volumetric analysis of mercuric compounds by a titration of the excess of sulphocyanide used for the precipitation. This conclusion was fully justified by experiment, and the method of analysis finally adopted was as follows:—

To a solution containing about 0·04 grm. of mercury in the form of a mercuric salt (chlorides must be absent owing to the use of silver nitrate in the titration) are added 10 cc. of decinormal ammonium sulphocyanide, and then excess of zinc sulphate solution. The precipitate is filtered and washed several times with dilute zinc sulphate. The filtrate is treated with 10 cc. of decinormal silver nitrate, and the excess of silver is determined in the usual manner by titration with decinormal sulphocyanide, employing ferric sulphate as an indicator. Working in this manner 1 cc. of sulphocyanide is equivalent to 0·005 grm. of mercury in accordance with the formula $ZnHg(CNS)_4$.

With smaller quantities of mercury it is advisable to employ N/20 solutions, in which case 1 cc. is required to precipitate 0·0025 grm. of mercury.

The method appears capable of considerable accuracy, and an estimation can be performed in less than five minutes. Excess of nitric acid does not influence the result, and hence the method may be applied to mercurous salts by first boiling with nitric acid and then diluting. For every 0·05 grm. of mercury there must be at least 10 cc. N/10 sulphocyanide, and care must be taken to have excess of zinc sulphate for precipitation. Further, it is advisable not to work at too great dilutions. It is essential that chlorides should be absent.

Balliol and Trinity College Laboratory, Oxford.

A POSSIBLE EXPLANATION OF THE INCREASE IN VISCOSITY WHICH RESULTS WHEN THE ALCOHOLS ARE MIXED WITH WATER, AND OF THE NEGATIVE VISCOSITY COEFFICIENTS OF CERTAIN SALTS WHEN DISSOLVED IN WATER.

By HARRY C. JONES and W. R. VEAZEY.

It is well known that when methyl or ethyl alcohol is mixed with water the viscosity of the mixture is much greater than that of either pure liquid. The following seems to us to be a possible explanation of this phenomenon:—

It was shown some time ago by Jones and Murray (*Am. Chem. Journ.*, 1903, xxx., 205) that when two associated liquids, such as formic acid and water, or acetic acid and water, and, probably, such as alcohol and water, are mixed, each diminishes the association of the other. The result would be that in such a mixture there would be present a *larger number of smaller molecules* than if the two liquids simply mixed without affecting each other's association.

This diminution in the association of the liquid molecules, increasing their number and diminishing their size, would increase the viscosity by increasing the total frictional surfaces of the molecules that would come in contact with one another—the smaller the molecules the larger the total surfaces of the molecules for a given mass of the liquid.

The above point can be illustrated by means of small shot and large shot. For a given mass, the smaller shot moving over one another would produce greater friction than the larger shot, due to the larger frictional surfaces that would come in contact. The same applies to the molecules of the mixed solvents.

The comparatively small association of the molecules of the mixed solvents explains another phenomenon which has manifested itself in a number of the investigations recently carried out in the Physical Chemical Laboratory, Johns Hopkins University (Jones and Lindsay, *Am. Chem. Journ.*, 1902, xxviii., 329; Jones and Carrol, *Ibid.*, 1904, xxxii.. 521; Jones and Bingham, *Ibid.*, 1905, xxxiv., 481; Jones and McMaster, *Ibid.*, 1906, xxxvi., 325). In those mixtures of solvents where the *viscosity is a maximum, the conductivity curve of many dissolved electrolytes shows a minimum.* As the conductivity curves, for the solutions of different concentrations of a given salt in different mixtures of two solvents, *approach the minimum, they approach one another.* This means that the molecular conductivities do not increase rapidly in these particular mixtures of the two solvents, with change in the dilution of the solution. This is exactly what would be expected if the molecules of the solvents in the mixture were only comparatively little associated. They would then have comparatively little dissociating power, and the conductivity in such a mixture of solvents would increase only slowly with increase in the dilution of the solution. The curves for molecular conductivity would therefore approach one another, as they approach the minimum.

It was observed in the course of our work that solutions of potassium sulphocyanate in water are *less viscous than pure water.* On looking up the literature that bears upon this problem, and especially the work of Wagner (*Zeit. Physik. Chem.*, 1890, v., 31), we find that a number of salts show this negative viscosity coefficient. They are potassium chloride, potassium nitrate, rubidium chloride, and cæsium chloride. Thallous nitrate also, apparently, shows the same phenomenon.

The explanation of this *negative viscosity coefficient* is comparatively simple, in the light of what has already been said in reference to viscosity.

The salts with the negative viscosity coefficient are, then, certain salts of potassium, rubidium, and cæsium. The case of thallous thallium will be considered a little later. If the *ions of the salt were very large*, relative to the molecules of the solvent, then the effect of the dissolved substance on the viscosity of the solvent would be to diminish it. This will be seen at once, if we think of a number of larger spheres mixed with a much larger number of smaller spheres. The frictional surfaces would be diminished, and, consequently, the friction, when these spheres move over one another.

The question is whether there is any reason to suppose that the ions of potassium, rubidium, and cæsium are large. If we turn to the curve of atomic volumes we find the answer (Lothar Meyer, "Die Moderne Theorien der Chemie"; Holleman, "Inorganic Chemistry"; Jones, "Elements of Physical Chemistry"). As is well known, potassium, rubidium, and cæsium occupy the maxima of the atomic volume curve, and these three elements have *much larger atomic volumes* than any other known elements.

The *qualitative* agreement of fact and theory are thus in accord, with the exception of the thallous salt. Since, however, we do not know at present the atomic volume of thallous thallium, this case will have to be left out of the discussion.

If we wish to test the above suggestion *quantitatively* we have the means of doing so. Potassium has a much larger atomic volume (about 47) than any other element except rubidium and cæsium. The atomic volume of rubidium is about 57, while the atomic volume of cæsium

is about 74. If we compare the viscosities of the same salt of these three elements, say the chlorides, we should expect to find, in terms of our hypothesis, that the viscosity coefficient would be less for rubidium chloride than for potassium chloride, and less for cæsium chloride than for rubidium chloride.

From the work of Wagner we can make the above comparison. The time of flow of pure water through the viscometer is taken as the unit of value for η. The values of η for normal solutions of potassium chloride, rubidium chloride, and cæsium chloride are :—

	η.
Potassium chloride	0·9872
Rubidium chloride	0·9846
Cæsium chloride	0·9775

It is worth noting that the difference between the values of η for cæsium chloride and rubidium chloride is much greater than the difference between rubidium chloride and potassium chloride. This is in keeping with the relative atomic volumes of the three elements. The difference between the atomic volume of rubidium and cæsium is much greater than the difference between the atomic volume of rubidium and potassium.

The question now arises whether, *e.g.*, all potassium salts show the negative viscosity coefficient. The answer is that they do not. The reason for this is obvious when we consider that the effect of a salt on the viscosity of a solvent is an additive function of both of the ions present in the solution. The anion, so far as we know, always tends to increase the viscosity of water, while certain cations, as those above considered, diminish the viscosity of water. The action of the salt, as a whole, upon the viscosity of water, is the algebraic sum of these effects, which may be either positive or negative.

Wagner (*Zeit. Phys. Chem.*, 1890, v., 36, 37) studied six salts of potassium in this connection, and found values of η less than unity only in the case of the chloride and nitrate. In the other four cases the action of the anion more than overcame the effect of the cation, and η was always greater than unity. *The chloride gave a negative value for* η. This would be expected, since *chlorine has itself a large atomic volume;* indeed, larger than that of any other elementary anion except bromine. This would, then, probably act in the same way as the potassium cation, giving a negative coefficient; or, if the coefficient due to chloride were positive, it would have a very small value.

For the same reason potassium nitrate shows a large negative viscosity coefficient.

If we extend the above conception to other cations with large atomic volumes, but with much smaller atomic volumes than the three alkalis, we shall find that it holds satisfactorily. Taking calcium, strontium, and barium, which, of all cations, have the next larger atomic volumes, and comparing their chlorides with respect to the values of η, we have, for normal solutions :—

	η.
Calcium chloride	1·1563
Strontium chloride	1·1411
Barium chloride..	1·1228

These values are all positive, as we should expect them to be, but their order is exactly *the reverse of the atomic volumes*, just as would be expected.

Chlorides with cations of still smaller atomic volumes have values of η much larger than the above. This will be seen from the following table, where all the values of η refer to normal solutions. In the same table are given the approximate atomic volumes of the cations of the several chlorides :—

	At vol.	η.
Magnesium chloride	14	1·2015
Cupric chloride	8	1·2050
Manganous chloride	7	1·2089
Nickel chloride	7	1·2055
Cobalt chloride	7	1·2041

It is obvious that for the atomic volumes of the same order of magnitude, the values of η are of the same order of magnitude; and, in general, the larger the atomic volume the smaller the value of η, just as we should anticipate in terms of our hypothesis.

The small values of η for zinc, cadmium, and mercury are probably due to the fact that the salts of these metals are only slightly dissociated.—*American Chemical Journal*, xxxvii., No. 4.

ULTRA-VIOLET LIGHT IN THE LABORATORY AND IN PRACTICE.*

By CHARLES BASKERVILLE.

Lenard, in 1900, noted that ultra-violet light may ozonise oxygen (*Ann. Phys.*, i., 486). The source of this light of short wave-length used by him was a spark-gap, the light being transmitted through quartz. It could be intercepted by sheets of mica.

Three years later, Goldstein, with liquid air, condensed ozone produced outside of Geissler tubes (*Ber.*, xxxvi., 3042). Unless the glass were permeable to the ultra-violet rays—that is, composed largely of quartz—no ozone was obtained.

The next year Warburg (*Ann. Phys.*, xiii., 475) found that during the silent electric discharge, the familiar method for producing ozone in a Siemens tube, ultra-violet light and cathode rays were obtained, and the production of ozone might be attributed to these rays.

This *savant*, in collaboration with Regener (*Sitzungsber. Preuss. Akad. d. Wiss.*, 1904, 1228), used a differential ozonometer with quartz capillary, and learned that not alone was an ozonising influence exercised by the ultra-violet light, but as well a de-ozonising.

Clement has shown that ozone is rapidly destroyed by increase in temperature (*Ann. Phys.*, 1904, xiv., 334). Fischer and Braehmer confirmed this (*Ber.*, 1905, xxxviii., 2633), and by using a quartz mercury lamp for the source of the ultra-violet light, demonstrated beyond question the ozonisation of oxygen under that influence. Manganese glass exposed a few hours to this ultra-violet light acquires the coloration observed in it after long exposure to sunlight.

These writers put forward the suggestion that ozone is formed in the higher portions of the atmosphere by the unabsorbed ultra-violet rays, sinks to lower regions, and is decomposed by oxidisable substances.

Regener (*Ann. Phys.*, 1906, xx., 1033) has determined that ultra-violet light rays of wave-length smaller than 200 $\mu\mu$ produce ozone, whereas the rays with wave-length of about 257 $\mu\mu$ or higher decompose it. Therefore we have a double action of the ultra-violet light. The apparently spontaneous de-ozonisation is similar to that of the influence of the elevation of temperature. An interesting and wide field of investigation is thus opened up for the study of the action of ultra-violet light of different wave-lengths. We have been using a mixture of reagents as it were.

Regener has also shown that the ultra-violet rays of small wave-length decompose ammonia, nitrogen monoxide, and nitrogen dioxide. Many chemical effects now known are manifested under the influence of the silent electric discharge. Nearly all gases and mixtures of gases (except the noble ones) are capable of at least one chemical reaction under its influence. It has been almost demonstrated that the silent discharge is similar to the action of ultra-violet light, and when that is definitely accomplished our knowledge of photographic chemical phenomena will have acquired a much broader field.

Ramsay and Spencer have recently studied some chemical and electrical changes induced by ultra-violet light (Chemical News, 1906, xciv., 77). An electroscope

* A Paper read at the Tenth General Meeting of the American Electro-chemical Society, New York, October 8, 1906.

charged positively is discharged by ultra-violet light; when negatively charged this does not occur. A conclusion was drawn from the work which indicates that elements and compounds, when illuminated by ultra-violet light, discharge corpuscles.

It has long been known that willemite (zinc orthosilicate) phosphoresces under the influence of ultra-violet light. If there be one thing in science that is attractive, it is the seeing of the invisible. Ever since, and even before the days when Cascariolo (in 1602) discovered what is now called "Canton's phosphorus," people have been actively interested in the phenomena of phosphorescence and fluorescence. It may be said to have eventuated in the discovery of radium.

Many natural substances have been found which glow in the dark under various influences. In the course of a prolonged study of the elaborate Morgan-Tiffany collections of gems and minerals in the American Museum of Natural History, Kunz and the writer exposed 13,000 specimens to ultra-violet rays. The light used was obtained by sparking a high-tension current among iron terminals in the lamp devised by Piffard. Only one or two of the many interesting observations will be noted here.

First, in examining the spodumenes, a new pink one obtained from California phosphoresced, showing a marked difference from the other varieties. This was proved to be new, and the beautiful gem has been named "Kunzite" in honour of my colleague in the investigations.

Second, one of the most phosphorescent minerals observed was colemanite. In the examination I was surprised to note that every mineral obtained from Mono Lake phosphoresced. These minerals obtained from other sources varied very much in their conduct. These do not crystallise alike, hence the phenomenon cannot be explained on that basis. They vary widely in their chemical composition, as may be seen from this list:—

Colemanite ..	$Ca_2B_6O_{11}.5H_2O$
Glauberite	$Na_2SO_4.CaSO_4$
Borax	$Na_2B_4O_7.10H_2O$
Polyhalite	$2CaSO_4.MgSO_4.K_2SO_4.2H_2O$
Halite	$NaCl$
Celestite	$SrSO_4$
Thenardite	Na_2SO_4
Gypsum	$CaSO_4.2H_2O$
Hanksite	$4Na_2SO_4.Na_2CO_3$
Northupite	$MgCO_3.Na_2CO_3.NaCl$
Pirssonite	$CaCO_3.Na_2CO_3.2H_2O$

Investigators of phosphorescent substances prepared in the laboratory have proved the need of some impurity in the material or the presence of something other than that looked upon as necessary to produce the actual chemical compound. This has been done in the case of the phosphorescent sulphides. Mr. Bourgougon, of this laboratory, has prepared willemite, pure zinc orthosilicate, and it does not phosphoresce, but with the addition of manganese and other metallic oxides in small amounts, splendid artificial willemite has been made. Humphreys has found the yttria earths in the fluorspars, and I have noted that chlorophane, the most responsive of all these fluorides, contains nearly 1 per cent of the yttria earths.

Someone has said that prophecy is the most gratuitous mistake, but to my mind there must be something not recognised in the ordinary analyses of those minerals from Mono Lake, and from them may come an element for a vacant place in Mendeleeff's table.

The artificial wollastonite (calcium metasilicate), and the pseudo-wollastonite made by Day and Allen show a marked difference under the influence of the ultra-violet light. The pseudo-wollastonite glows in the dark and may be readily separated from the normal preparation.

On account of the brilliant response willemite gives to the ultra-violet light, at my suggestion it has been placed in the concentrating rooms of the New Jersey Zinc Co., where large quantities of that mineral are prepared for the furnace daily. A perfect control is thus had over the waste in the tailings.

We frequently use the lamp in the laboratory for the examination of precipitates, before and after burning. I am inclined to think it will serve a greater purpose, as has been indicated.

THE ACTION OF SODIUM ON ACETONE.*

By RAYMOND FOSS BACON and PAUL C. FREER.

(Concluded from p. 246).

Experiment 8.—Four grms. of diatetone alcohol were dissolved in 20 cc. of ethyl alcohol and 20 cc. of water. The solution was saturated with sodium acetate and 4 grms. of semicarbazide hydrochloride were added. The solution was then rendered very faintly alkaline, and placed in ice-water for one hour, being vigorously scratched with a glass rod. No precipitate appeared. To be sure that the conditions were correct for the formation of a semicarbazone, the solution was divided into two equal portions. To portion number two, 2 grms. of acetone were added, whereupon a precipitate of crystalline needles immediately appeared. Four grms. of semicarbazide hydrochloride were now added to this portion of the original solution, so that a sufficiency of the reagent should be present to precipitate all acetone and all diacetone alcohol, should it form a semicarbazone. Both the original, unchanged portion and the second one were kept in the ice-chest overnight. In the morning, portion number one, to which no acetone had been added, contained a very faint precipitate (0·01 grm. melting at 185° to 186°, it being acetone semicarbazone), so that a very small amount of acetone had been separated by hydrolysis. From portion number two, 2·5 grms. of acetone semicarbazone were isolated, melting at 186°.

From the above result it is evident that the acetone semicarbazone obtained in the preceding experiments could not have originated in the sodium derivative of diacetone alcohol, as the hydrolysis of the latter body is a time reaction which proceeds slowly.

The above results confirm the previous work in every way, and establish the fact that the action of sodium on acetone gives a sodium derivative which can only be sodium acetone.

In view of the above conclusions it is not deemed necessary further to discuss Miss Taylor's results, as, apparently, she had not reproduced the conditions under which Freer worked. A very short review of some of the chief facts established in the earlier literature, and which Miss Taylor appears not to have considered, may not be out of place, as it will serve to recall some of the arguments which were not discussed in Miss Taylor's paper. The portion of the product of the action of sodium on acetone which is insoluble in ether was shown by Freer (*Am. Chem. Journ.*, 1893, xv., 592) to consist of acetone sodium, sodium isopropylate, and disodium pinaconate, the soluble portion, of a sodium derivative of acetone; no sodium isopropylate was isolated from this soluble portion, and, if it is not carefully acidified, mesityl oxide and phoron are to be obtained. In studying the products of the action of chlorcarbonic ether on sodium acetone, Miss Taylor suggests that a mixture of ethyl isopropyl carbonate and diethylcarbonate would yield 34 per cent of carbon dioxide, whereas Freer found 33·89 per cent on decomposing the oil boiling between 128° and 129°, and produced by the interaction of sodium acetone and chlorcarbonic ether (calculated CO_2 for $C_6H_{16}O_3$, 33·84 per cent), but Miss Taylor appears to have overlooked the statement that Freer also proved the presence of ethyl alcohol and *acetone* in the products left after saponification (*Ibid.*, 1891, xiii., 325). If acetone had been present as mesityl oxide,

* From the *Philippine Journal of Science*, ii., No. 1.

the percentage of carbon dioxide would have fallen very much. It was further shown by Freer that the fraction boiling at 128° yielded a sufficient amount of acetone on decomposition with dilute acid to allow of its being separated as the acetone sodium-bisulphite compound (*Ibid.*, 1895, xvii., 11). (Found, carbon dioxide, 33·7 per cent; the quantity of ethyl alcohol was less than one-half the organic liquid isolated, it boiled at 78°). We would therefore, if we were dealing with a mixture of diethylcarbonate, ethyl isopropyl carbonate, and mesityl oxide, need to assume a large proportion of the latter substance to be present, and this would inevitably have lowered the carbon dioxide very markedly. Furthermore, the oil boiling between 132° and 137° yielded 30 per cent of *acetone* (calculated 48·8 per cent), and this figure, because of the difficulties in quantitative estimation, is undoubtedly too low. It does not seem reasonable to assume that an oil which would contain a sufficient quantity of mesityl oxide to yield so much acetone would not further react with phenylhydrazine, but, on the other hand, this percentage would correspond to a total of 62 per cent of the isoacetone ester in the oil. Miss Taylor's supposition is that this acetone comes from mesityl oxide present in the mixture. If enough mesityl oxide occurred in the mixture to yield 30 per cent of acetone, then the carbon dioxide found would be reduced by 11 per cent, to say nothing of the change brought about in the analytical results. A mixture which consists of ethyl isopropylcarbonate, diethylcarbonate, and sufficient mesityl oxide to yield 30 per cent of acetone, and which will also give 33·7 per cent of carbon dioxide, can not be calculated. Miss Taylor allowed her reaction product to stand over phenylhydrazine for four days. It is possible that, if isopropenylethylcarbonate was present at all, it would by that time have reacted with phenylhydrazine; it is also possible that, owing to some variation in her work, Miss Taylor never had the body in the oil she prepared. Attention is further called to the fact that Freer obtained enough 2-chlorpropene by the action of phosphorus pentachloride to isolate this very low-boiling substance. The reaction product also absorbs bromine in the cold, without yielding hydrobromic acid.

Miss Taylor did not use benzoyl chloride in studying the composition of sodium acetone, substituting *p*-nitrobenzoyl chloride therefor. Again, in her reactions she does not seem to have had a sodium derivative which acted like the one described above, for she obtained *none of the addition products* described by Freer as a result of the action of benzoyl chloride on sodium acetone. That *p*-nitrobenzoyl chloride might not form an isoacetone ester is conceivable, but in that event it *should* give addition products. Freer, in studying the action of benzoyl chloride on sodium acetone separated the reaction products into two parts, one soluble in alkalis, the other insoluble. In this instance, the insoluble oil (12 grms.) boiling at 120° (39 mm. pressure) added bromine in the cold, gave acetone in sufficient quantity to be isolated from the sodium-bisulphite compound, isopropyl alcohol, and ethyl alcohol. The organic liquid containing the acetone was twice as great in volume as the remainder. The portion of the reaction product which was soluble in alkalis yielded acetophenon, *mono-*, and *dibenzoyl* acetone. Here we are not dealing with a mixture of oils, but with crystalline solids which can be isolated in the pure state. It is difficult to see how mono- and dibenzoyl acetone could result from a mixture of condensation products of acetone, sodium isopropylate, and caustic soda. Sodium acetone must have taken part in the reaction.

It should also be remembered that Freer and Lachman (*Am. Chem. Journ.*, 1897, xix., 878) studied the action of sodium on methyl propylketone, obtained 22·1 per cent of sodium in the derivative (calculated, 21·3 per cent), isolated dibenzoyl methyl propylketone, and from 2 grms. of the alkali insoluble portion obtained 0·9 grm. benzoic acid, 1 grm. methylpropylketone, some halogenated oil, and some hydrochloric acid. The entire 2 grms. is therefore accounted for. Intermediate halogenated addition products were also demonstrated.

Pure mesityl oxide reacts so energetically with sodium that the products may take fire with explosive violence, the sodium compound is so unstable that it can not be isolated.

From the above considerations it is evident that the original descriptions of sodium acetone remain unaltered.

Note.—Since the above was written an article by Levi and Voghera (*Gazz. Chim. Ital.*, 1905, xxxv., I., 277) has come to our attention. These investigators studied the electrolysis of KSCN, KI, and NaI in acetone solution, water being rigidly excluded from their solutions. At the cathode sodium acetone respectively potassium acetone separated as white substances. With water these gave acetone and sodium, or potassium hydroxides. The potassium acetone gave 40·70 per cent of potassium (calculated, 40·62 per cent), and it dissociated, when placed in water, into acetone, potassium, and hydroxyl ions, the correct lowering of the freezing-point for a molecular weight of 96 was obtained (found, 95·3).

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part II.—Analysis of the Silver, Copper, and Tin Groups.

By Arthur A. Noyes and William C. Bray.

(Continued from p. 243).

Analysis of the Tin Group.

Procedure 41.—Dilute in a small flask the first portion of the ammonium sulphide solution (P. 22) with about 20 cc. water, make it distinctly acid with HCl, and warm it slightly for five minutes with frequent shaking to coagulate the precipitate. (Fine, not flocculent, white or pale yellow precipitate, absence of *tin group*; deep yellow or orange flocculent precipitate, presence of *tin group*). Treat the second portion of the ammonium sulphide solution (P. 22) in the same way, and unite the precipitate, if considerable in amount, with the first one. Filter out, and wash the precipitate, using suction, finally sucking it as dry as possible. (Precipitate, P. 42; filtrates, reject).

Notes.

1. Much time is saved by determining at this point whether or not any element of the tin group is present. When ammonium monosulphide has been used, there is usually no difficulty in drawing a definite conclusion in regard to this from the size and appearance of the HCl precipitate; for in the absence of the tin group only a very small, nearly white precipitate of finely divided sulphur separates. When, however, ammonium polysulphide has been used, it may not be possible to decide as to the presence or absence of a small quantity (1 to 5 mgrms.) of arsenic, antimony, or tin; for not only is a fairly large precipitate of sulphur then obtained, but it may be darkened in colour by the presence of CuS or HgS; yet when the precipitate is nearly white, and finely divided or granular, the conclusion can be drawn at once that no element of the tin group is present in quantity as large as 1 mgrm.; and when it has a pronounced yellow colour (indicating arsenic or tin) or an orange-red colour (indicating antimony) the conclusion can be drawn that one of these elements is present. In this connection it may be mentioned that a mixture of SnS_2 and Sb_2S_5 does not always have a colour intermediate between those just mentioned, but may be brown or dark grey.

2. When however, the HCl precipitate from a polysulphide solution is fairly small, and is dark brown (indicating copper), or dark grey or black (indicating mer-

* From the *Technology Quarterly*, xix., No. 3, September, 1906.

cury or one of the rarer elements), or of unpronounced yellow or orange colour, so as to make any conclusion as to the tin group doubtful, the precipitate is best treated as follows:—Heat it with 15 to 20 cc. NH_4OH (0·96) almost to boiling for five minutes, and filter; test the precipitate for copper by P. 23, 28, and 30 if it has not already been found present; add to the filtrate a few drops of ammonium monosulphide, filter out any precipitate, heat the filtrate to boiling, make it acid with HCl, shake, filter out the precipitate, and treat it by P. 42 as usual. The character of the HCl precipitate thus obtained will clearly indicate the presence or absence of the tin group; for by the treatment with NH_4OH the excess of sulphur originally present and any CuS is left undissolved, and by the $(NH_4)_2S$ added to the solution any mercury present is precipitated, so that the HCl precipitate can contain only sulphides of the tin group and a very little sulphur. As_2S_5, Sb_2S_5, and SnS_2 all dissolve in NH_4OH (though in the cases of Sb_2S_5 and SnS_2 less abundantly than in ammonium sulphide), owing to the formation of a mixture of salts of the intermediate sulpho-acids, such as H_3AsO_3S and $H_3AsO_2S_2$. The addition of $(NH_4)_2S$ to the NH_4OH solution, and the heating serve to convert these into more highly sulphurated acids, from which HCl will then precipitate the simple sulphides completely. The incidental removal of the small amounts of CuS and HgS by the NH_4OH treatment is not necessary as far as the analysis of the tin group is concerned, since their presence does not interfere with the detection of even 1 mgrm. of arsenic, antimony, or tin; but it does enable 1 or 2 mgrms. of copper to be detected which might otherwise be lost.

3. When the HCl is added to the solution of the sulpho-salts, the corresponding sulpho-acids which are liberated decompose immediately into H_2S and the solid sulphides, which are now necessarily in the higher state of oxidation, since the lower sulphides, if originally present, have been oxidised by the polysulphide. The fact that the sulpho-acids decompose while the sulpho-salts are stable is a consequence of the Mass Action Law, which, when applied to the dissociation of the complex anions taking place according to the equations, $SnS_3^{=} = SnS_2 + S$, $2AsS_4^{=} = As_2S_5 + 3S^{=}$, $2SbS_4^{=} = Sb_2S_5 + 3S^{=}$, evidently requires that these decompose to a greater extent into the un-ionised sulphides (SnS_2, &c.) the smaller the concentration of the $S^{=}$ ion in the solution. Now in the solution of the largely ionised $(NH_4^{+})_2S^{=}$ there is a fairly large concentration of $S^{=}$ ion; but when the solution is made acid with HCl, the $S^{=}$ ion is, for the most part, converted by the relatively large concentration of the H^{+} ion into the slightly ionised substances HS^{-} and H_2S; and, consequently, the concentration of the un-ionised sulphides in the solution becomes great enough to exceed the solubility value, and the solid sulphides separate out.

Procedure 42.—Transfer the precipitated sulphides dried by suction (P. 41) to a wide test-tube, add from a small graduate exactly 10 cc. HCl (1·20), and heat nearly but not quite to boiling (preferably by immersing the test-tube in hot water or on a steam-bath) for about ten minutes with frequent stirring. Add 5 cc. water from a graduate containing 40 cc. water, filter, wash once with about 5 cc. water from the graduate, collecting this wash-water with the filtrate; remove the filtrate, and add to it the water remaining in the graduate; wash the residue with HCl (1·12). (Residue, P. 43; filtrate, P. 45).

Notes.

1. If a much weaker HCl solution than the acid of specific gravity 1·20 is used, or if the acid becomes diluted by an unnecessary quantity of water left in the precipitate, much Sb_2S_5 will be left undissolved. Even with the strong acid some Sb_2S_5 may remain undissolved, especially when a large quantity is present, in which case the residue if small in amount will have an orange colour. This small quantity of Sb_2S_5 would be only very slowly removed by further treatments with HCl; it does not, however, interfere with the subsequent tests for arsenic. Moreover, when only a small quantity of Sb_2S_5 is originally present, a large proportion of it is extracted, so that it will not escape detection. Sb_2S_5 dissolves with formation of $SbCl_3$ and liberation of sulphur; SnS_2 with formation of $SnCl_4$.

2. If the solution be kept just below the boiling-point during the treatment with HCl, the amount of As_2S_5 which dissolves in ten minutes is insignificant; but this is no longer true if the solution be allowed to boil, for the boiling rapidly expels from the solution the H_2S liberated from the other sulphides or by slight decomposition of the As_2S_5 itself, and thus enables the decomposition of the latter to proceed further.

3. As_2S_3 is more rapidly dissolved by HCl than is As_2S_5. If the former can be present in the precipitate, which can occur only when HNO_3 or aqua regia was not used in dissolving the original substance, and if ammonium monosulphide was employed for separating the copper and tin groups, the procedure should be modified as follows:—After the addition of HCl to the sulphides saturate with H_2S in the cold, and then heat nearly, but not quite, to boiling for ten minutes, passing a slow current of H_2S gas through the mixture. Under these conditions scarcely any As_2S_3 dissolves.

4. About 5 cc. water are added to the HCl solution to enable it to be filtered. If more be added, and the H_2S has not been completely expelled from the solution, a precipitate of Sb_2S_3 may separate. If this happens after the filtration, it does, of course, no harm.

5. Care must be taken to follow closely the directions in regard to the quantities of HCl and water used; for the subsequent separation of antimony and tin (P. 45) depends upon a proper concentration of the acid.

6. The greater part of any CuS and HgS present will be dissolved by the HCl, and will be precipitated later with the Sb_2S_3 (P. 45). A little remains with the As_2S_5, but this does not interfere with the tests for arsenic. *Of the precipitates of the rarer elements, PtS_2, Au_2S_3-6, Se, and MoS_3 are dissolved by the HCl scarcely at all, and TeS_2 only to a small extent. The dissolving of the last, like that of As_2S_3, can be entirely prevented by passing a slow current of H_2S through the hot HCl solution.

Procedure 43.—Warm the residue from the HCl treatment (P. 42) with 5 to 10 cc. HCl (1·12) adding solid $KClO_3$ in small portions until the reaction is complete; filter off the sulphur, and evaporate the solution to about 2 cc. [If the solution is still distinctly yellow, or if a yellow precipitate has separated, test for and remove platinum by *P. 43*a*, and treat the filtrate as follows]. Add NH_4OH gradually until the solution after shaking smells of it; cool, filter off, and reject any precipitate. Add to the filtrate about one-third its volume of NH_4OH (0·90), and several drops of magnesium ammonium chloride reagent, and shake. If no precipitate appears, rub the walls of the test-tube gently with a glass rod for a minute or two. (White crystalline precipitate, presence of *arsenic*). Collect the precipitate on a filter, and wash it once with NH_4OH (0·96). (Precipitate, P. 44; filtrate reject, or test for gold, selenium, tellurium, and molybdenum, by *P. 43*b*).

Notes.

1. The main reaction between $KClO_3$ and concentrated HCl is the formation of Cl_2; the yellow colour results from the formation of a small proportion of chlorine dioxide, ClO_2.

2. As_2S_5, though only very slowly dissolved by HCl alone, is dissolved rapidly by it in the presence of Cl_2, because of the destruction of the H_2S, one of the reaction products, by oxidation. It is dissolved with formation of

H_3AsO_4; $AsCl_5$ has never been shown to exist. When, as here, arsenic is present in the higher state of oxidation, solutions of it may be boiled without loss of an amount of arsenic significant in qualitative analysis.

3. A white precipitate, obtained on adding NH_4OH may arise from the presence of mercury. The NH_4OH solution may contain not only arsenic, but also certain rare metals, and the small quantities of copper (if ammonium polysulphide was used), antimony, and stannic tin that were not dissolved out of the sulphide precipitate by HCl.

4. The test for arsenic depends on the formation of magnesium ammonium arsenate, $Mg^{++}(NH_4)^{+}AsO_4^{=}$. This salt is somewhat soluble in water, and therefore the solution tested should be fairly concentrated. Owing to hydrolysis (into NH_4OH and $Mg^{++}HAsO_4^{=}$), the precipitate is much more soluble in water than in a strong NH_4OH solution; hence the addition of a large quantity of the latter. Like other crystalline precipitates, it tends to form a supersaturated solution. Precipitation is promoted by agitation, by rubbing the walls of the tube with a glass rod, and by increasing the degree of supersaturation, which is done by concentrating and adding NH_4OH. Provided these precautions are taken and the total volume of the final solution does not exceed 5 cc., the presence of even half a mgrm. of arsenic can be detected. Care must be taken not to scratch the glass by violent rubbing, since the powdered glass may be mistaken for the $MgNH_4AsO_4$ precipitate.

5. The magnesium ammonium chloride reagent contains $MgCl_2$ and NH_4Cl. The presence of the latter salt prevents the precipitation of $Mg(OH)_2$ by NH_4OH, by reducing the OH^- concentration.

**Procedure* 43*a*.—Evaporate the solution of the sulphides in HCl and $KClO_3$ (P. 43) until KCl crystallises out, cool, and add water drop by drop until the KCl just re-dissolves. (Yellow precipitate, presence of *platinum*). Filter, wash the precipitate with a little cold saturated KCl solution, and treat the filtrate by P. 43 to detect and remove arsenic. Dissolve the precipitate by pouring repeatedly a 5 to 10 cc. portion of hot water through the filter, and add to the solution a few drops of KI solution. (Deep red colour, presence of *platinum*).

Notes.

1. Potassium chlorplatinate, $K^{+}{}_2PtCl_6^{=}$, is fairly soluble in water, but much less so in a saturated KCl solution, owing to the common ion effect.

2. The deep red colour formed on the addition of KI to K_2PtCl_6 is due to the formation of K_2PtI_6 in solution. When the K_2PtCl_6 is present in excess a black precipitate of PtI_4 separates, but this dissolves readily on further addition of KI.

**Procedure* 43*b*.—To the filtrate from the $MgCl_2$ precipitate (P. 43) add 2 to 3 cc. saturated oxalic acid ($H_2C_2O_4$) solution, and evaporate in a casserole to 3 to 4 cc. to expel the excess of ammonia. Make the solution slightly acid with $H_2C_2O_4$, if it is not already so, add about 10 cc. water, and digest on a steam-bath for several minutes. (Purple precipitate, presence of *gold*). To the mixture add 2 to 3 cc. HCl (1·12) to dissolve any tellurium hydroxide, and filter. (Precipitate, reject; filtrate, *P. 43*c*).

Notes.

1. Metallic gold is precipitated readily from a solution of ammonium oxalate only when the solution is hot and slightly acid; but even under these conditions the precipitation is complete only after several minutes. If these conditions are not realised, several mgrms. of gold may escape detection.

2. The more powerful reducing agents, H_2SO_3 and $SnCl_2$, also precipitate gold, but they reduce selenium and tellurium (and mercury) compounds as well.

**Procedure* 43*c*.—Evaporate the filtrate from the $H_2C_2O_4$ precipitate (*P. 43*b*) almost to dryness, add 10 cc. HCl (1·12), and filter off any KCl that has separated. Collect the filtrate in a test-tube, add about 0·2 grm. solid Na_2SO_3, and allow the mixture to stand for at least five minutes, adding more Na_2SO_3 if the SO_2 odour disappears. (Red precipitate, presence of *selenium*). Filter. (Precipitate, reject; filtrate, *P. 43*d*).

Notes.

1. By the action of H_2SO_3 on selenous acid (H_2SeO_3) in the cold a voluminous red precipitate of selenium is quickly formed; but the reaction is complete only after several minutes. When the solution is hot the more compact black modification of selenium is obtained; but the test is then less delicate and less characteristic.

2. Tellurium is reduced by H_2SO_3 in moderately dilute HCl solutions, but not at all when the concentration of the acid is as great as that of specific gravity 1·12. Selenium, however, separates completely from a more concentrated acid, as well as from a more dilute one. For these reasons, though a greater concentration of HCl is unobjectionable, a lesser concentration would cause the precipitation of tellurium and obscure the selenium test.

**Procedure* 43*d*.—Dilute the filtrate from the H_2SO_3 precipitate (P. 43*c*) with an equal volume of water, and add a few drops of KI solution and a little solid Na_2SO_3. (Black precipitate, presence of *tellurium*). Filter after a few minutes. (Precipitate, reject; filtrate, *P. 43*e*).

Notes.

1. As stated in *P. 43*c*, N. 2, tellurium is precipitated by H_2SO_3 alone when the HCl solution of specific gravity 1·12 is diluted somewhat with water, especially if the mixture is kept hot. The precipitation, however, is much more rapid, and is complete after a few minutes even in the cold if KI is also present. KI alone does not reduce tellurium compounds, but precipitates black TeI_4, which dissolves somewhat in excess of KI, forming a deep red solution of K_2TeI_6. The advantage of adding KI is that the iodine compound of tellurium is more rapidly reduced by H_2SO_3 than is the chlorine compound or tellurous acid itself.

2. Selenous acid is immediately reduced to selenium by KI in HCl solution; but this element is completely precipitated by H_2SO_3 in *P. 43*c* if the directions there given are followed; even if not so removed, it would give a red precipitate, not a black one.

3. Molybdic acid by this treatment is also slowly reduced to a lower compound, which remains in solution. Iodine may thereby be liberated and even precipitated after all the H_2SO_3 has been oxidised. For this reason the solution should not be allowed to stand for more than half-an-hour before filtering.

**Procedure* 43*e*.—Boil the filtrate from the KI precipitate (*P. 43*d*) until the SO_2 is expelled, cool the solution, add 3 or 4 cc. 10 per cent KCNS solution and some granulated zinc. (Red colour, presence of *molybdenum*). [If it is desired to form a better estimate of the quantity of molybdenum present, treat the solution as described in N. 4].

Notes.

1. The H_2SO_3 is boiled out, since otherwise sulphur would be precipitated by the action of zinc.

2. The red colour is due to the formation of $Mo(SCN)_4$, corresponding to MoO_2, an intermediate stage in the reduction of molybdic acid (H_2MoO_4) by the zinc. The colour may appear before the addition of zinc, since the H_2MoO_4 may have already have been partially reduced by H_2SO_3 and HI. Long continued action of zinc causes the red colour to disappear; for the chloride, $MoCl_3$, corresponding to the oxide, Mo_2O_3, to which H_2MoO_4 is finally reduced, gives a colourless solution with KCNS.

3. Ferric salts also give a red colour with KCNS; but a coloration arising from the presence of iron as an impurity disappears almost immediately on the addition of zinc, owing to reduction to the ferrous state.

4. It is difficult from the depth of the red coloration to form an estimate of the quantity of molybdenum present. The molybdenum may be obtained in the form of a precipitated sulphide by treating the solution to which KCNS and zinc have been added as follows:—Add a little solid $KClO_3$, and boil to re-oxidise the molybdenum, and finally to expel the chlorine, adding more HCl (1·20), if necessary; pass H_2S into the solution for ten minutes, keeping it near the boiling-point.

Procedure 44.—Dissolve the $MgCl_2.NH_4Cl$ precipitate (P. 43) by pouring a little HCl (1·12) through the filter, heat the solution obtained nearly to boiling, and pass in H_2S for at least five minutes, keeping the solution hot. (White precipitate turning yellow, presence of *arsenic*). (Precipitate and solution, reject).

Notes.

1. The slow formation in a dilute acid solution of a pale yellow precipitate with H_2S is a characteristic test for H_3AsO_4. The precipitate is a mixture of As_2S_5, As_2S_3, and sulphur, the amount of As_2S_5 being comparatively small in the presence of strong HCl and at high temperatures.

2. A considerable amount of H_2S may be absorbed by a dilute H_3AsO_3 solution before any precipitate appears. This is due to the formation of H_3AsO_3S, which then decomposes slowly, giving H_3AsO_3 and sulphur. This last decomposition may be accelerated by increasing the H+ concentration, and by raising the temperature. The H_3AsO_3 formed reacts at once with H_2S, and As_2S_3 is precipitated. The reactions taking place are, therefore, $H_3AsO_4 + H_2S = H_3AsO_3S + H_2O$, $H_3AsO_3S = H_3AsO_3 + S$, $2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$, which together give the reaction—

$$2H_3AsO_4 + 5H_2S = As_2S_3 + S_2 + 8H_2O.$$

The rate of this reaction depends upon the rate of the slowest of the single reactions—the decomposition of H_3AsO_3S. As_2S_5 is produced by an independent reaction, $2H_3AsO_4 + 5H_2S = As_2S_3 + 4H_2O$, which takes place very slowly.

Procedure 45.—Heat the solution of the sulphides (P. 42), which should contain 10 cc. HCl (1·20) in a total volume of 50 cc., to about 90°, and pass in H_2S gas for about five minutes, keeping the solution at about 90°. If no precipitate appears, add about 5 cc. water, and again saturate with H_2S at the same temperature as before. (Orange-red precipitate, presence of *antimony*). Filter while hot, add 5 cc. water, heat the filtrate nearly to boiling, again saturate with H_2S to ensure complete precipitation of antimony, and filter if any precipitate forms. Wash the precipitates with hot water. (Precipitate, P. 46; filtrate, P. 47).

Notes.

1. By following carefully the directions given in P. 42 and this procedure, a good separation of antimony and tin may be obtained; when only 1 mgrm. of antimony is present it is precipitated as Sb_2S_3, while even 500 mgrms. of (stannic) tin give no precipitate. If, however, the HCl solution be too concentrated, a small quantity of antimony will escape detection; hence the precaution of adding a little water to the solution and repeating the treatment with H_2S. If the HCl solution be too dilute, or if it be not kept hot, some SnS_2 may precipitate when a large amount of tin is present. When mixed with a little Sb_2S_3 a brown precipitate results.

2. If mercury or copper be present in the substance and ammonium polysulphide has been used, HgS or CuS may be precipitated at this point as a grey or black precipitate.

Procedure 46.—Dissolve the H_2S precipitate (P. 45) in a little strong HCl in a small casserole, and evaporate the solution to about 1 cc. Introduce beneath the solution a piece of platinum-foil, and place upon it a piece of pure tin. After several minutes wash carefully with water, and cover the platinum-foil with (alkaline) NaOCl solution. (Black deposit on the platinum undissolved by NaOCl, presence of *antimony*). Precipitate and solution, reject).

Notes.

1. Mercury and copper, if present, will also be precipitated in the metallic condition upon the platinum, but the antimony may be easily distinguished from them by its black colour. Tin is used rather than zinc in precipitating the antimony, since zinc would also precipitate tin from the solution.

2. The treatment with NaOCl serves to prove that the black precipitate does not consist of arsenic or tellurium; for these elements are readily dissolved by it, while antimony is not. Since, however, several mgrms. of arsenic must be present before the treatment with tin would give a deposit on the platinum, an arsenic deposit will probably never be obtained in an actual analysis.

Procedure 47.—Cool the filtrate from the H_2S precipitate (P. 45), dilute with 20 cc. water, and pass in H_2S for ten minutes. (Yellow precipitate, presence of *tin*). If there is a precipitate, evaporate the mixture without filtering to 5 to 10 cc., add about 1 grm. of granulated zinc, and allow the action to continue for several minutes, but not until all the zinc is dissolved. (Grey, spongy precipitate, presence of *tin*). Decant the solution into a test-tube, allow any particles suspended in it to settle out, decant again, and unite the two residues. Heat the residues with 2 to 5 cc. HCl (1·20) until everything (except any particles of carbon is dissolved. Dilute the solution with one-half its volume of water, and pour it at once through a small filter into 5 cc. $HgCl_2$ solution. (White precipitate, presence of *tin*).

Notes.

1. The solution is precipitated with H_2S in the cold, because a small quantity of SnS_2 would not separate from a hot solution unless the acid were more diluted. The addition of much water is avoided, since it has to be evaporated off in the confirmatory test.

2. In the confirmatory test the precipitate of SnS_2 is not filtered off, but is dissolved by concentrating the acid by evaporation, since it clogs the filter and tends to pass through it. The zinc must not be allowed to dissolve entirely, since the tin might then also dissolve. Care must also be taken not to lose it in the process of decantation or by failing to dissolve it completely. Finally, since $SnCl_2$ oxidises rapidly in the air, the solution in HCl must be immediately added to the $HgCl_2$ solution. If these precautions are observed, the presence of half a m.grm. of tin in the HCl solution of the sulphides (P. 4) may be detected after some practice. The confirmatory test is, however, less delicate than the precipitation by H_2S, but it is more characteristic, since $SbCl_3$, even if present, does not reduce $HgCl_2$.

(To be continued).

Chemistry and Photographic Exhibition. — The above Exhibition, which is being held in Gamage's Main Bazaar Hall, opened on Monday, May 27, and will remain open till Saturday, June 8. It is open from 9 a.m. to 8 p.m.; Saturdays, 9 a.m. to 5 p.m. Admission is free. Stands have been fully taken up by leading manufacturers.

Constitution and Properties of Boron Steel.—Léon Guillet.—Normal boron steels consist of a solid solution of iron and boron, containing very little boron, perlite, and a special substance which seems to be a boro-carbide of iron, containing only a little carbon. This last compound seems to make the steel very brittle, but this effect disappears after tempering, when the substance itself dissolves,—*Comptes Rendus*, cxliv., No. 19,

THE RAPID DETERMINATION OF NICKEL IN STEEL.*

By Dr. GEORGE T. DOUGHERTY, Chicago, Ill.

For the past ten years the quickest standard method generally used, at least in the United States, for the determination of nickel in steel has been by making, as a preliminary step, a separation of the mass of the iron from nickel by means of ether and then repeating the process. This method was probably first described by G. H. Chase, of Philadelphia, and was a distinct advance toward simplified and rapid nickel analysis. What small quantity of iron remains along with the nickel after the two ether treatments is finally removed by ammonia, and a great many chemists make a second precipitation of this iron with ammonia to make sure that all the nickel is saved for a determination. These many operations with repetitions necessarily take a good deal of the busy analyst's time. It seems to be the fashion with many to prolong the work by evaporating to dryness the preliminary solution of the sample and to take up and filter off the silica, when all this is unnecessary and superfluous, especially when nickel in solution is to be finally titrated with potassium cyanide solution.

The separation with ether cannot very well be applied to the analysis of ores of the kinds usually carrying nickel, owing to the presence of sulphuric acid, which has displaced the other acids used in decomposing the ore at the start. The standard method for ores, therefore, is to make two precipitations with ammonia and one basic acetate precipitation. Basic acetate separations are usually tedious affairs, and with many persons rather difficult and not uniformly successful, besides imposing an unwieldly quantity of liquid on the operator's hands to filter and handle.

The Use of Ammonia.

The ether method for nickel in steel, when all essential details are properly and carefully attended to, makes for highly accurate results. However, not being quite satisfied with it on account of the time required, I began experiments under different conditions with ammonia and ammonium chloride for separating nickel from iron. These require many months' time to go thoroughly into the subject. Many chemists of repute one after another tried the ammonia treatment and were disgusted with the results, which would show only 20 to 70 per cent of the quantity of the nickel known to be present. One writer of international note says that it takes at least six precipitations with ammonia to get out all the nickel. They always ascribed their failures to the absorption of nickel by the ferric hydrate precipitate. It occurred to me that perhaps they had not used quite enough ammonia or ammonium chloride or both.

To start the experiments I had nickel steels of known nickel contents, which I had determined carefully by using the standard ether method, and finally titrating with potassium cyanide solution. The idea was to try with successively larger quantities of hydrochloric acid, subsequently neutralised by ammonia, to form ammonium chloride and different quantities of free ammonia in excess after neutralisation. For example, I began with 15 cc. of hydrochloric acid added to the solution of 1 grm. of nickel steel solution in one test; 25 cc. in the next; 50, 75, and finally 100 cc. hydrochloric acid, and tested the filtrate each time by titrating with potassium cyanide, running all tests in duplicate or more. In view of the numberless failures reported with ammonia and ammonium chloride for a complete separation of nickel, all I could hope for was to find a minimum quantity of ammonium chloride and ammonia which will separate the largest percentage of nickel present, and under similar conditions will yield a fairly constant percentage of this element present. On the basis of the average results thus obtained I could build up a proper correction to be added to the actual figures obtained in analysis, and thus approximate the true result as closely as possible. It was therefore an agreeable surprise when I finally discovered that 100 cc. strong hydrochloric acid (plus 10 cc. acid used in dissolving the steel), subsequently neutralised with ammonia (or its equivalent, 75 grms. of ammonium chloride) and 50 cc. free ammonia added in excess, after carefully neutralising the solution, will make a perfect and complete single separation, leaving no trace of nickel in the ferric hydrate precipitate. To save the time and labour of washing the bulky iron precipitate, the liquid—after precipitating with ammonia—is diluted to 500 cc. and filtered on a large dry filter, and 250 cc. of filtrate is taken for titration. These remarks have reference to 1 grm. of steel weighed off for analyses; that is, 75 grms. of ammonium chloride, or its equivalent of hydrochloric acid and ammonia, will separate 100 per cent of the nickel present from 1 grm. of steel, and the same proportion of ammonium chloride and ammonia will probably hold good whether for ½ grm. or for 2 grms. of steel, though if 2 grms. of steel were attempted it would become a white elephant on one's hands on account of the double quantities of chemicals, &c., required. Then the 500 cc. volumetric flask would not be large enough to hold all, and a 1000 cc. flask and a larger filter and funnel would have to be used. One grm. of steel is amply sufficient for accurate close results by the new method, though 2 grms. usually are taken when the ether method is used.

The capacity of the new method is considerably above that of the standard ether method. By the former, one can make two or three determinations in the time required for one by the older method. The details of the new method, as finally adopted by myself, are as follows:—

The New Method in Detail.

Dissolve 1 grm. of steel drillings in 15 cc. nitric acid (specific gravity 1·20) in a small beaker and boil one minute. Have ready and hot 270 cc. ammonium chloride solution containing 75 grms. in a 500 cc. common thin glass flask. Pour the steel solution into this flask, adding rinsings from the beaker. Add hydrochloric acid if necessary to clear up, and then ammonia, little by little, until the solution, though practically clear, is so dark from the dissolved ferric hydrate that you cannot quite see through the body of liquid in the flask when you hold it in front of you before the window, the top part being rather more transparent. (This neutralisation is the critical point of the process; a little under neutralising or over neutralising is apt to cause lower results). Cool the flask and contents quickly by running against the glass cold water from the faucet or standing in a vessel. Transfer the contents of this flask, with a little rinsing, into a 500 cc. volumetric flask; add all at once 50 cc. ammonia (sp. gr. 0·90), whirl, and fill up with water to the mark. Shake vigorously to mix thoroughly, and pour through a 10-inch filter in a 4-inch ribbed funnel into a clean dry 600 cc. flask. Take 250 cc. of filtrate (½ grm. of sample), transfer it to a No. 4 Griffin beaker, throw in it a bit of litmus paper, and add sufficient hydrochloric acid (it will take about 25 cc.) to acidify the liquid when litmus paper has turned from blue to red; add ammonia cautiously (about ½ to 1 cc. at a time), stirring with the glass rod until the litmus paper becomes blue again. Take out the litmus paper and rinse it slightly and throw it away. Not more than 1 cc. ammonia in excess is allowable. It is not desirable to allow the litmus paper to remain in the liquid, for when disintegrated by continuous stirring during the subsequent titration its scattered fibres often obscure and render a little uncertain the end-point of the titration. Cool by standing in a large vessel of cold water. When cool, add 5 cc. of silver nitrate solution (0·10 grm. in 200 cc. water, and then 5 cc. of a 2 per cent solution of potassium iodide). Stir and titrate with standard potassium cyanide solution until the very last drop dissipates and destroys the white opacity of the liquid, making it perfectly clear. One can best avoid over-titrating by sitting down and looking horizontally on the body of

* From the *Iron Age*, April 25, 1907.

liquid in the beaker while titrating and stirring. Deduct 0·2 cc. from the burette reading and multiply by 2, and by the titre or nickel factor of the cyanide solution.

If dry ammonium chloride is not in stock it can easily be made up by pouring into a 500 cc. common thin glass flask, wiped dry on the inside, 80 cc. water and 100 cc. strong hydrochloric acid, and with caution and frequent shaking 100 cc. strong ammonia, slanting the flask during the addition. This mixing of hydrochloric acid and ammonia causes a sudden and high rise of temperature (up to 90° or 95° C., nearly boiling hot), and must not be done in volumetric flasks of the usual thick glass, which is not well calculated to withstand extreme changes of temperature and quick cooling under the faucet without liability to crack.

If no particular accuracy of results is required this method may be considerably quickened by having the cold ammonium chloride solution in the 500 cc. volumetric flask when the solution of steel is added to it, and the whole neutralised and precipitated with 50 cc. ammonia and diluted to the mark, or the neutralising is omitted and 55 cc. ammonia at once added to the acid mixture of steel solution and cold ammonium chloride solution. In either modification of the method (neutralising cold and no neutralising attempted) the results are a little irregular and low, falling sometimes as much as ten points under the truth; for example, 3·58 per cent on a 3·68 per cent nickel steel. Scarcely any better results can be obtained by neutralising hot and at once precipitating and filtering while yet hot, and taking 250 cc. of the filtrate after heated back to the same temperature as the 500 cc. liquid had shown on the thermometer at the time of filtering. Only by neutralising hot and cooling the neutralised liquid before precipitating and filtering will the results be uniformly close and fully up to the truth.

(To be continued).

NOTICES OF BOOKS.

Elementary Practical Chemistry. By FRANK CLOWES, D.Sc. (Lond.), and J. BERNARD COLEMAN, A.R.C.Sc. Fifth Edition. London: J. and A. Churchill. 1907.

THE fifth edition of this text-book of elementary practical chemistry is for the first time published in two separate volumes, in order to meet the wishes of many teachers and students. The first volume contains a course of elementary chemistry, such as the student of science should work through before beginning his chemical work. The subject is treated in such an order that an instructive progressive course of lecture work could be founded upon it, and full directions are given for the performance of the practical work, so that the book could quite safely be put into the hands of the beginner. The second volume deals with qualitative analysis, together with some simple quantitative work, both gravimetric and volumetric. A new section on the preparation of pure specimens of metals, their oxides and hydroxides, and salts, gives details of such preparations as the student could with profit carry out at various stages during his course.

Theories of Chemistry. By SVANTE ARRHENIUS. Edited by T. SLATER PRICE, D.Sc., Ph.D., F.I.C. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

IT is impossible to read this book without reflecting that the students of the University of California in Berkeley, before whom the lectures it contains were delivered in the summer of 1904, were singularly fortunate. If merely reading the lectures is sufficient to arouse the interest to a remarkable degree, which will undoubtedly be the experience of all who open the book, it would be difficult to over estimate the enthusiasm aroused when to the charm of the matter and style was added the influence of the personality of the lecturer. The aim of the lectures was to give a complete and coherent account of the development of theories in general chemistry, linking the present with the past, and showing how out of the old grew the new. The book is written in such a style that it can be read with profit by the student whose knowledge does not extend beyond that covered by the average first year course, while to many teachers it will bring fresh ideas or fresh aspects of old knowledge, and all will be struck by the philosophical and liberal spirit displayed in every page. The subjects discussed include the electrical forces between the atoms, the composition of the atoms, and the theory of electrolytic dissociation—one lecture being devoted to objections to this theory and problems connected with it which are still to be solved.

Elektrometallurgie der Eisens. ("The Electro-metallurgy of Iron"). By Dr. BERNHARD NEUMANN. Halle-a-S.: Wilhelm Knapp. 1907.

THE author of this monograph has collected enough material relating to the electrical method of extracting iron to enable him to draw very important conclusions as to its practicability. By carefully comparing the technical and economic results of several of the more important processes, he has formed the opinion that in countries such as England and Germany, where the coal supply is abundant and the ores are impure, the electrical method cannot, at any rate under present conditions, hope to compete with the old process. On the other hand, in Canada and South America, where there is a lack of fuel, the iron ores are pure, and water power is easily procured, he believes that the electric furnace method has a great future before it. In order to prove these assertions, he has given in the monograph a complete account of the more important processes which have been patented for the reduction of iron ores by carbon in the electric furnace; beginning with the earliest methods which were suggested, and tracing the development of modern processes. The report of the Canadian Commission is quoted freely, and the preparation of alloys of iron in the electric furnace, which appears to be a rapidly growing industry, is treated fully. The monograph is one of the first to give a complete survey of all the work that has been done in this region and its technical results, and will be found to contain information of great commercial value.

Il Secolo XIX.: La Fisica e l'Elettroteenica. ("The Nineteenth Century: Physics and Electro-technology"). By FRANCESCO GRASSI. Milan: Francesco Vallardi.

IN this book the progress which various branches of physics and electro-technology made in the Nineteenth Century is reviewed, in a style which should commend itself to anyone who is contemplating the delivery of popular lectures, or to the youth with a turn for science and an interest in its development. The number of subjects which the author attacks in one volume of moderate size precludes the possibility of his giving more than a superficial account of any of them; but while nothing very new is contained in the book, it has some special features which are worthy of mention. One of these is the illustrations, which are very copious and in some cases peculiarly interesting; for example, the reproductions of old diagrams and pictures, in which the curious contrivances of the early philosophers are shown. The portraits of men of eminence in the scientific world, together with their autographs, also add to the interest of the book, which is a good example of a familiar type of popular work.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 18, May 6, 1907.

Extension of Friedel and Craft's Reaction.—A. Haller and A. Guyot.—Tertiary aromatic amines, and also certain secondary amines, such as diphenylamine, can condense with a great number of organic molecules in presence of aluminium chloride. According to the conditions under which the reaction is carried out—the temperature, the proportion of aluminium chloride, the excess of one or other of the reagents—different products of condensation are obtained. The yields are generally very high. When indigotin and dimethylaniline are used, the product is $C_{32}H_{30}N_4O$, resulting from the union of one molecule of indigotin with two of dimethylaniline, with the elimination of one molecule of water. The condensation occurs similarly with other reagents, *e.g.*, orthodibenzoyl benzene and dimethylaniline, ethyl phenylglyoxalate and dimethylaniline, &c. In all the cases investigated by the author, with the exception of the oxalic ethers, the molecules contain one or more ketonic or quinonic carbonyl groups, and the aluminium chloride seems to act by fixing the amine molecules on these carbonyl groups, transforming them into tertiary carbinols, $>C<^{OH}_{C_6H_4-NR_2}$, with the subsequent elimination, in certain cases, of one or more molecules of water. Condensations with aluminium chloride often occur when zinc chloride has no action.

Direct Hydrogenation of Carbamines. — Paul Sabatier and A. Mailhe.—When gaseous methylcarbamine, $CH_3.N:C$, is driven by an excess of hydrogen upon reduced nickel kept at 160° to 180°, hydrogenation proceeds regularly. The resulting product, which is condensed in a cooled U-tube, consists chiefly of dimethylamine, and contains also small quantities of ethylamine and diethylamine. When ethyl carbamine, $C_2H_5.N:C$, is hydrogenated in the same way the greater part of the product is methylethylamine, $^{C_2H_5}_{CH_3}>NH$, together with small quantities of propylamine and dipropylamine. The carbamine corresponding to trimethylcarbinol, $(CH_3)_3C.N:C$, when similarly treated, gives the substance $^{CH_3}_{(CH_3)_3C}>NH$, which is a colourless liquid boiling at 58—60° and behaving like a secondary amine. These results show that when the above carbamines are subjected to hydrogenation by means of nickel at temperatures below 180°, one portion polymerises to form tarry products, another portion forms the isomeric nitrile $R.CN$, which then yields amines, $R.CH_2.NH_2$ and $(R.CH_2)_2NH$, and free ammonia, while the greatest part undergoes the reaction $R.N:C+2H_2=^{R}_{CH_3}>NH$. If the temperature applied is too high (220—250°) much ammonia is produced, and also hydrogen mixed with hydrocarbons.

Absolute Atomic Weight of Bromine.—Gustavus D. Hinrichs.—Baxter found for the atomic weight of bromine Br = 79·952 if Ag = 107·93. But if Ag is taken as the standard, and put = 108, and Br = 80, the ratio Ag + Br : Ag = 1·74074. If Br = 80·1 this value becomes 1·74169, or the change is +95 units of the fifth decimal place for an increase of 0·1 in the atomic weight. Baxter's eighteen determinations give 1·74079, which exceeds the calculated value by five units. Therefore the mean atomic weight exceeds 80 by $5\times\frac{100}{95}=5{\cdot}2$ approximately. Hence Baxter's determinations give for the mean value Br = 80·0052. The difference is lower than the actual degree of accuracy of the determinations, and hence Baxter's work confirms the value 80 for the absolute atomic weight of bromine.

Decahydro-α-naphthylacetone and Decahydro-α-naphthylamine.—Henri Leroux.—Already noticed.

Inactive Dilactylic Acid.—E. Jungfleisch and M. Godchot.—When sodium ethyl lactate is treated with ethyl α-bromopropionate, ethyl dilactylate is formed :—

$$CH_3-CH(ONa)-CO_2-C_2H_5 + CH_3-CH(Br)-CO_2-C_2H_5 =$$
$$= CH_3-CH(O-CH-CH_3)-CO_2-C_2H_5 + NaBr.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad CO_2-C_2H_5$$

This dilactylate is saponified by boiling alcoholic soda, forming sodium dilactylate, from which the free acid may be liberated by means of sulphuric acid. When the free acid is distilled, even *in vacuo*, it loses one molecule of water and is transformed into dilactylic anhydride, which is isomeric with dilactide. This method of preparing lactylic acid is general and can be applied to other compounds.

MEETINGS FOR THE WEEK.

Monday, June 3rd.—Society of Chemical Industry, 8. "The Nature of, and Changes involved in the Production and Setting of Plaster-of-Paris," by W. A. Davis. "Analysis of White Lead," by W. A. Davis and C. A. Klein. "A Calorimeter for Volatile Liquid Fuel, specially adapted for Petrol," by W. H. Rawles. "Influence of Temperature of Dyeing on Resolution," by W. P. Dreaper and A. Wilson. "Loss of Nitre in the Chamber Process," by J. K. H. Inglis.

— — Royal Institution, 5. General Moothly Meeting.

Tuesday, 4th.—Royal Institution 3. "Malaria, Sleeping Sickness, Tick Fever, and Allied Diseases," by Prof. G. H. F. Nuttall, F.R.S., &c.

Wednesday, 5th.—Society of Public Analysts, 8. "Horse Fat and 'Animal' Oil," by H. Dunlop. "Method for Determining Caustic Lime in Fertilisers," by J. Heodrick. "Rapid Estimation of Total Solids in Milk," by C. Revis. "The Reducing Action of Hydrogen—III., The Reduction of Molybdic and Vanadic Acids," by A. C. Chapman and H. D. Law.

Thursday, 6th.—Royal Institution, 3. "Chemical Progress—Work of Berthelot, Mendeleeff, and Moissan," by Prof. Sir James Dewar, F.R.S., &c.

— — Chemical, 8.30. "Relation between Absorption Spectra and Chemical Constitution—Part VII., Pyridine and some of its Derivatives," by F. Baker and E. C. C Baly. "Interaction of Methylene Chloride and the Sodium Derivative of Ethyl Malonate," by F. Tutin "Molecular Weight of β-Naphthol in Solution in Solid Naphthalene," by E. P. Perman and J. H. Davies. "Synthesis of Hexatriene Derivatives," by I. Smedley. "Constitution of the Diazo-compounds," by J. C. Cain. "*p*-Cresol Sulphoxide and Sulphide," by S. Smiles and T. P. Hilditch. *p*-Dioxyphenylsulphoxide," by S. Smiles and A. W. Bain. "Coloured Azo-derivatives of 1 : 3-Diphenylbarbituric Acid—Dynamic Isomerism among the Hydrazones of 1 : 3-Diphenylalloxan," by M. A. Whiteley. "Dibromoaminoazobenzene," by J. T. Hewitt and N. Walker.

Friday, 7th.—Royal Institution, 9. "Studies in High Vacua and Helium at Low Temperatures," by Prof. Sir James Dewar, F.R.S., &c.

Saturday, 8th.—Royal Institution, 3. "The Contest between Guns and Armour," by Sir William H. White, K.C.B., F.R.S., &c.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2480.

ON THE THERMO-CHEMISTRY OF FLAME SPECTRA AT HIGH TEMPERATURES.*

By W. N. HARTLEY, F.R.S., D.Sc., Royal College of Science, Dublin.

The majority of the metallic elements have two distinct spectra, one of lines the other of bands. In some spectra, bands are the most prominent feature in association with but few lines; in others the lines predominate over the bands. Of those substances with bands in their spectra there are many which may be reduced in quantity to almost a minimum without the bands disappearing from the flame or from the uncondensed spark; from this it would appear that there is a very intimate relationship between the bands and lines of the same element. It has been supposed that such bands as cannot be attributed to definite salts are the spectra of oxides or even of hydrides, but many facts have been accumulated from which it is evident that this is not correct. On the other hand, many of the elements which possess complex molecules may readily be understood to emit molecular or band spectra, but some further explanation is necessary when the molecule of the element is monatomic.

The present communication deals only with one part of this subject, being merely a record of observations on high temperature flame reactions, and principally those of the alkali and alkaline earth metals. The spectra of the alkali metals at the highest temperature in the flame of the oxy-hydrogen blowpipe more nearly resemble those obtained from the arc than any other spectra of the same elements. Thus, all the lines of lithium photographed by Kayser and Runge in the arc have been obtained in the flame from lithium nitrate. This is evidence of the high temperature obtainable in the flame, but if further evidence were desired, we have it in the great facility with which both gold and silver can be vapourised and condensed from the vapour, the large number of arc lines of iron, practically all those that are reversible, which appear in the flame, and the volatilisation of palladium and iridium in weighable quantities.

Part I.—Band Spectra of the Alkali and Alkaline Earth Metals.

Lenard (*Ann. der Physik*, 1905, [4], xvii., 197) has recently described the coloured glow emitted by globules of fused salts in the Bunsen flame, the particular parts of the flame from which the glow emanates, with the spectrum of the glow from different metals.

The spectra of the glow from metallic vapours have been photographed repeatedly in the oxyhydrogen flame spectra of all the alkali metal salts ("Flame Spectra at High Temperatures," *Phil. Trans.*, 1894, clxxxv., A, 161), and those of the alkaline earths, but Lenard states that he has not been able to find the maximum of brightness of the continued rays of potassium, at or near λ 5500, as it appears on the reproduction of my photographs (Plates 6 and 7). On referring to the plate, I do not see that the maximum is at λ 5500, and the strong continuous rays are so evenly distributed over so wide a range of spectrum that it is better to refer to the letterpress of the publication.

The continuous spectrum of lithium extended from about λ 4600 to λ 3200; of sodium very strongly from λ 6020 to λ 3600 and continued weakly to λ 3320; of potassium it was intense from about λ 4600 to λ 3400, but continuous rays were observed from about λ 5700. As importance has been attached to the kind of photographic plate used, it is as well to state that isochromatic plates of Edwards's or of the Ilford make, and Cadett and Neall's spectrum plates, were most generally in use, but when the plates were not isochromatic, the fact was recorded on the photograph. On the photograph referred to by Lenard, the plate was less sensitive to the green than to the orange and red rays, so that a weak space is seen between λ 5359 and λ 5200. The continuous spectra have been carefully examined on more than forty different photographs of the alkali metal salts, including sulphates, nitrates, carbonates, and chlorides; also potassium cyanide, ferrocyanide, ferricyanide, and fluosilicate.

A hitherto undescribed feature in the spectra which is unquestionably due to each metal, is the occurrence of a multitude of bands in the rays of lithium, sodium, and potassium, which occupy spaces within the above-quoted wave-lengths.

The photographed spectra of potassium chloride, as emitted by different flames, were studied. In no case did the nature of the salt, the support used, or the nature of the flame, make any difference, except in lengthening or shortening the exposure which, *during comparatively short periods*, was proved to have the same effect as putting more or less of the salt into the flame.

It is deemed of importance that this should be recorded, because different metals, and also different salts of the same metal, under the same conditions show different results, and this arises principally from the difference in volatility of the salts, or the comparative ease with which they are thermo-chemically decomposed. It is also important that the salts be pure, otherwise the spectrum of one may interfere with the other, the two spectra become confused, and the bands are not visible.

Lithium Salts.—Various specimens of the sulphate, carbonate, chloride, and nitrate were used, but most of the spectra were photographed from the nitrate. Latterly the salts obtained have been so pure that the sulphate showed hardly a trace of any other metal, even sodium, and no calcium. (These salts were kindly presented to me by Mr. W. E. B. Blenkinsop, the Managing Director of the firm of May and Baker, Ltd., of Garden Wharf, Battersea, London). They show all the lines attributed to lithium by Kayser and Runge. The structure of the background is that of fine lines and very narrow bands extremely close together, extending from λ 3466 to λ 4677. But it must be observed that a feeble group of the water-vapour lines may be seen on other spectra extending to λ 3466; therefore to be sure that these may not be mistaken for lithium bands, it is better to place the margin of the latter below λ 3610 and to disregard the rays of greater refrangibility. The lithium bands, therefore, without doubt, extend from λ 3610 to λ 4677. The lithium spectrum exclusive of the lines, is a very weak one, so that an extended band of continuous rays is more often photographed than a discontinuous spectrum consisting of a multitude of fine lines and narrow bands.

Sodium Salts.—The banded spectrum of sodium has been observed on three photographs, but it is only feebly visible. A complete array of the bands was photographed from very pure rock salt, and from a specially prepared pure sodium chloride. Like the lithium bands, they are very narrow and close together; they extend from rays a little less refrangible than λ 3700 down to about λ 4800. A beautiful banded spectrum has recently been photographed from sodium carbonate in the oxyhydrogen blowpipe flame. Some feeble lines accompany the bands, and the principal lines D^1 and D^2 are enormously extended on each side so as to form a broad band. O. H. Basquin (*Astrophys. Journ.*, 1901, xiv., 1) observed a series of lines in the spectrum of the sodium arc when surrounded by an atmosphere of hydrogen; they lie between λ 5000 and 3800. "This is probably a complicated fluting of heads of bands, less clearly marked than usual, and running towards shorter wave-lengths." It is more than probable that the bands which I have observed are of the same nature as

* A Paper read before the Royal Society, January 31st, 1907. (Revised March 22nd).

those which he, by the aid of a large concave grating, resolved into lines.

(In lieu of any better hypothesis Basquin supposed that the banded spectra of several of the metals, including sodium, are due to hydrides being formed in the arc. Sodium hydride cannot exist in a state of vapour; it readily undergoes dissociation, which commences at 200°, and is complete at 422°, under ordinary barometric pressures; the bands, therefore, are not due to sodium hydride).

There is an important difference between the spectrum of sodium taken from the metal when burnt in a Bunsen flame and that obtained in the oxyhydrogen blowpipe flame, but it appears to be due solely to the lower temperature of the former. With metallic sodium, no lines but the principal yellow ones are visible; these are very broad and dense. It is extremely difficult to introduce sodium into the oxyhydrogen blowpipe flame, because it melts so readily and escapes. The sodium spectrum from salts gives not only the D^1 and D^2 lines more widely extended on either side than is the case with the metal, but also the subordinate series of lines, the band of continuous rays, and with the highest temperature of the flame, the series of bands in these rays in addition.

Potassium Salts.—The potassium bands are very easily photographed from many different salts. They are themselves wider, and also wider apart than those of lithium and sodium, and the structure of the banded spectrum varies greatly with the quantity of the substance used and with the exposure given. Many lines accompany the stronger banded spectrum.

The potassium bands, as obtained from weighed quantities of potassium chloride, frequently extend from λ 3600 to λ 4800. This effect is obtained from 0·05 grm. of the salt, but with 1 grm. or an exposure of five minutes, the bands may stretch down into the red. With an exposure of one and a-half minutes there is barely an indication of bands, and when the quantity of the chloride is reduced to 0·025 grm., there is nothing but a continuous spectrum to be seen. Potassium cyanide and ferrocyanide with the same exposure both yielded very dense spectra, but on that account the bands are not seen distinctly. They are well seen in spectra photographed from potash-alum, potassium carbonate, and potassium ferricyanide. Between the wave-lengths of two cadmium lines, 4800·8 and 4414·5, ten of these bands were counted. They are not sharp at the edges, and the spaces between successive bands decrease as they tend towards the violet. They appear, in fact, like a continuation of the subordinate series of lines, 4808·8, 4803·8, 4796·8, 4788·8, and 4759·8 (Liveing and Dewar), but they are diffuse. There is an absence of any accompanying fine lines such are seen in the lithium and sodium spectra. Spectra from sodium and potassium carbonates have recently been photographed with Wratten and Wainwright's panchromatic spectrum plates, which give the lines well defined with the continuous rays from wave-lengths 7699·3 and 7665·6 of potassium to a line 3303·1 which belongs to sodium. There is a strong band in the red, extending from λ 6911 to λ 7350, fading away rather abruptly on the less refrangible side, but with feeble continuous rays extending to λ 7665·6. The bands mentioned above are seen to be composed of two groups; the one nearer the red appears like the continuation of the subordinate series of lines with the spaces between them decreasing, and the second group more towards the violet, where the bands do not appreciably vary in width or in distance apart.

Rubidium Salts.—Sulphate and chloride of great purity yielded merely a continuous spectrum in which there are no bands, but the lines are very broad and strong.

Cæsium Salts.—The same effect is seen with the corresponding salts of cæsium.

Banded Spectra from the Alkaline Earth Salts.

The banded spectra observed with barium chloride and strontium sulphate are reproduced, but with a dispersion of only one prism on Plate 6, in "Flame Spectra at High Temperatures" (*Phil. Trans.*, 1894). In course of a study of the oxyhydrogen flame spectra of calcium, strontium, and barium compounds, made in 1902, bands were constantly observed in minerals containing barium, just as the bands of lead are constantly seen in the flame spectra of minerals containing lead, and, subsequently, the barium bands were photographed from the flame spectra of very carefully prepared compounds which were spectroscopically pure.

The bands in the continuous background of rays are different from those of the alkali metal group. In calcium and strontium the most conspicuous bands are broad and disposed somewhat irregularly, but in detail the spectra of calcium, strontium, and barium compounds show bands of two varieties, the one broad overlying narrow bands; when the quantity of material is small, only the narrow bands are seen, and when the slit is not narrow enough they appear as diffused rays or a continuous spectrum. As in the lithium, sodium, potassium group, the calcium, strontium, and barium spectra differ much in intensity, and follow in the same order as the alkali metals in this respect, which is that of the numerical values of the atomic weights of the metals, the higher the value the greater the volatility of the compound. The strontium and barium chlorides exhibit the banded spectra best, but they are well seen also in sulphates, carbonates, and oxides. The best mineral in which to study the bands of calcium is the natural sulphate, selenite. It should not be overlooked that compounds yield their own spectra, such as chlorides, under certain conditions, phosphates, and fluorides, as, for instance, ferrous phosphate and calcium fluoride. The oxides B_2O_3 and P_4O_{10} also emit their own spectra, but whereas the former shows bands the latter shows lines only. This has been made the basis of a method of separating alkali metal flame spectra from those of the alkaline earth metals (*Trans. Chem. Soc.*, 1893, lxiii., 138). Bands characteristic probably of the sulphates may be found to overlie the metal bands.

Several different compounds of barium have all been found to yield the same banded flame spectrum when a sufficient quantity of substance is introduced into the flame, and all strontium salts also yield in like circumstances the same flame spectrum. When the sulphates of the alkaline earths are submitted to the oxyhydrogen flame, they all yield the banded spectra, and in the case of calcium and strontium sulphates, also certain lines in addition, but barium sulphate frequently shows only the bands without the barium line; therefore, the lines appear more readily than the bands with calcium salts, and the bands more readily than the lines with barium compounds. In fact, barium behaves in this respect very much as lead does.

There is an important difference in the chemical nature of the three sulphates after being heated in the flame; thus, the barium sulphate is entirely reduced to sulphide, so that we arrive at the fact that the same spectrum is common to chloride, oxide, and sulphide. But the chlorides are converted by the water-vapour in such a flame into oxides, so that we have simply the oxide and sulphide to consider.

The strontium sulphate is reduced partly to oxide and partly to sulphide under precisely the same conditions, and the calcium salt is simply converted into oxides. As the oxide produced from the chloride and sulphide produced from the sulphate of barium yield exactly the same banded spectrum, it is evident that we are dealing with the spectrum of the only constituent in common, which is the metal. It is quite inconceivable that the oxide and sulphide should give identical spectra of the respective compounds because the molecular weights of the compounds are different. The same observation applies to the compounds of strontium, which yield spectra with lines and bands, but we know that strontium sulphate, after it has been removed from the flame, has by less than one-half been reduced to sulphide; it is therefore probable that in this case, as in that of barium, the spectrum is caused either by the dissociation

of the sulphide in the flame or by a chemical reduction. Calcium sulphate is not simply deoxidised in the flame, like the corresponding salts of strontium and barium, but is converted into lime, yet this compound exhibits both lines and bands.

Evidence of Thermo-chemical Reduction of Refractory Oxides in the Flame.

It has already been shown that aluminium can be reduced from its oxide in the oxyhydrogen flame, that it colours the flame, and emits the two lines λλ 3967 and 3946. It was concluded that bands which have been attributed to the oxide are in reality metal bands ("Banded Flame Spectra of Metals," p. 346, and Plate XXXI.). Bands of beryllium and lanthanum were also reduced from their oxides; the greater volatility of metallic beryllium caused the band spectrum to be photographed without the lines. (This was observed by Pollok in its reduction by the arc).

I have now arrived at the conviction, from additional evidence presently to be adduced, that calcium and strontium are also produced in the oxyhydrogen flame by thermo-chemical reduction of their oxides and sulphides.

The question of the reduction of the oxides of the dyad and triad groups is quite different from that of the oxides of the alkali metals, because compounds of the latter are not only easily volatilised, but it has been proved by Ste.-Claire Deville that in the manufacture of the alkali metals, the oxides are thermo-chemically dissociated, and then reduced by carbon entering into immediate combination with the dissociated oxygen.

Spectro-chemical Evidence from Anhydrous Flames and Dehydrated Salts.

By an anhydrous flame is meant, one in which water is not a product of combustion. Any salt which yields the spectrum or imparts the characteristic colour of the metal to such a flame, is excluded from the view of Arrhenius that vapourised salts are first hydrolysed by water-vapour in the flame, that the hydroxides thus formed undergo ionisation, and the spectra are caused by the metallic cations. Smithells, Dawson, and Wilson first applied this test to alkali salts, by heating them in the flame of burning cyanogen (*Proc. Roy. Soc.*, 1899, lxiv., 142). Lenard also has observed that sodium salts colour the flame of carbon disulphide. The authors aforesaid suggest that a chemical reduction takes place, and the metal then colours the flame. I have extended this inquiry by placing anhydrous salts in the flame of carbon monoxide. Smithells has shown that, if this gas be carefully dried, it will not inflame when issuing from a jet, but if the jet be heated the gas ignites. It has also been shown that carbon monoxide stored over water in a gas-holder will not inflame in air if the jet be small like that of a Bunsen or ordinary "bat's wing" burner, but it will burn from a tube if the orifice be wide enough, and even from a "bat's wing" burner when the pressure is small; though in these latter circumstances the flame is very small (see Hartley, "On the Temperature of certain Flames," *Trans. Chem. Soc.*, 1896, lxix., 844). In view of these facts, pure carbon monoxide was most carefully dried, first with a column of pumice saturated with oil of vitriol, and then with two large tubes of phosphoric anhydride.

The gas was conducted into a platinum tube with an internal diameter of 6 mm. and a length of 30 cm. It was found that under these conditions the gas was very difficult to inflame, but it did burn; nevertheless, to increase the temperature and render the same steady by ensuring combustion, the tube was heated red-hot by a Mecke burner placed 3 inches from its orifice.

On introducing into the flame recently ignited carbonates of lithium, sodium, and potassium, even without heating the platinum tube, beautiful spectra were observed, such as are visible in the flame of a Bunsen burner. It was very difficult to see the red line of potassium about λ 7660, but the green glow and a group of green lines about λ 5800 were observed. Experiments were tried in both the inner and outer cones, but only when the substance was heated at the tip of the inner cone could the group of green lines be seen. In this instance it is not reasonable to suppose that sufficient water could gain access to the flame to give rise to hydrolysis, and, in fact, hydrolysis could not take place.

The same experiments were repeated with the oxides, carbonates, nitrates of calcium, strontium, and barium; but although the platinum tube was heated to bright redness, there was no trace of a spectrum of either bands or lines in any case. Calcium, strontium, and barium chlorides, on the other hand, showed superb spectra of the chlorides, apparently identical with those produced by heating the same salts in a coal-gas flame saturated with hydrochloric acid. The temperature of this carbon-monoxide flame, which was from 50 to 75 mm. long, is higher than that of a Bunsen burner of the same size (*loc. cit.*), and can raise a larger mass of material to a higher temperature. (Platinum wire 1/40th mm. in thickness can be melted into a globule in any part of the flame). Here we have evidence that the metals of the alkalis behave quite differently from those of the alkaline earths; calcium, strontium, and barium chlorides are volatile without decomposition, for they fuse and remain clear liquids without showing turbidity for as long as is necessary to observe their spectra. Inasmuch as they appear to yield their own spectra, they behave like calcium fluoride when placed in the oxyhydrogen blowpipe flame, and doubtless other similar fluorides and phosphates. The most important facts ascertained so far are, first, the alkaline earth oxides are not volatile in the carbon-monoxide flame, or, if they are, they show no spectrum; second, the flame is a powerful reducing one to all oxides with a heat of formation not greater than that of zinc oxide, but the oxides in question are not reduced; thirdly, the temperature of the flame is higher than that of a Bunsen burner, and over a large area it is nearly as high as that of the oxyhydrogen flame; fourthly, the chlorides are volatile in an anhydrous flame, but the stability of the chlorides in such a flame is somewhat doubtful, as they may undergo dissociation.

The action of the cyanogen flame is very different from that of the flame of carbon monoxide, because cyanogen is a very powerful reducing agent.

When calcium oxide was introduced on a platinum-wire into the flame of cyanogen burning in air, there was no action low down in the flame, but when the substance was placed at the tip of the inner cone, there was a magnificent display of the same spectrum as that seen when calcium metal is burnt in air, and with no trace of the cyanogen bands. The effect on baryta was tested in a similar manner, by making pure barium carbonate into a stiff paste with water, and moulding it round a loop of platinum-wire. On placing this in the flame at the same point, an equally fine spectrum of barium was obtained. In both instances the spectra were identical with those photographed when the same compounds were placed in a Mecke burner, but the brilliancy and intensity of the rays were greatly increased.

Beyond all doubt these spectra are the spectra of the metals.

The deductions from these facts are, that the lines and bands seen in the oxyhydrogen flame are certainly not the spectra of the oxides, because if the difference between this and the carbon monoxide flame were simply one of temperature, the emission spectra of oxides and sulphides should be quite as easily produced in a carbon monoxide flame as in one of hydrogen. Finally, carbon monoxide was burnt with oxygen in a Deville blowpipe, and still no spectrum of calcium or strontium was seen, except when traces of chloride were present. The salts were supported on very thin slips of Donegal kyanite.

The presence of hydrogen in the flame is therefore a necessary element in some chemical reaction which leads to the reduction of the sulphides or oxides to the metallic

state. The temperature of these flames, which can melt platinum, is sufficient to effect the thermo-chemical dissociation of water-vapour, and it is probable that in this lies the cause of the spectra appearing.

Spectra of the metals observed in a carbon monoxide flame on the grandest scale are those which were photographed from the Bessemer "blow," but in this case the spectra are not due to the heating of a substance in a pure gas or even in a mixture of gases, but are the result of the internal combustion of impurities in the metal, which causes the vapours to be carried off in a stream of intensely heated carbon monoxide mixed with nitrogen and a small proportion of hydrogen, all of which gases, except the nitrogen, are burnt in the air. The average vapour pressure of water in the blast amounts to about 1 *per cent* of the air; this is reduced by the metal bath to hydrogen and carbon monoxide, and, as the temperature is an exceedingly high one, it is not surprising that a line spectrum of calcium seen in the oxyhydrogen flame has been photographed in the Bessemer flame, the flame being a mixed hydrogen and carbon monoxide one. The lines are, however, only two, namely, 4226·9 and 4581·6. Arguments from Bessemer flame observations rather lead to confusion, on account of the many other elements present in the flame, and they must therefore be rejected or treated with discrimination.

It will be observed that in the groups Li, Na, K, and Ca, Sr, Ba, the facility with which the bands are produced increases with the atomic weights, likewise the volatility of metals increases in the same order, and as, in the first group, the elements are monatomic, the relative vapour densities are half their atomic weights; accordingly we have 7·2, 23·2, 39·2 as the relative quantities of matter in the flame if they have all the same volatility, and if their oxides undergo dissociation with equal facility; but the least easily dissociated is the least volatile lithium oxide; we may therefore say that the vapour pressure of potassium will be at least six times that of lithium in any flame in which the two oxides are placed under the same conditions. As there is very little difference between the heats of formation of the groups of oxides, CaO, SrO, and BaO, the energy required for their reduction may be considered to be the same for each oxide. The respective volatilities of the oxides or of the metals is not known, neither are we acquainted with their vapour densities; accordingly we may assume them to be either monatomic or diatomic molecules; if the latter, then the relative quantities of vapour in the flame will be in the proportion of the atomic weights, or 40·87·6, and 137·4; if they are monatomic, half these quantities, which gives three and a-half times as much vapour of barium in the flame as of calcium, under the same conditions in either case. If, however, we attempt to compare the vapour densities of the alkali metals with those of the dyad group as judged by their spectra, we are at once met with a difficulty by the reactions in the flame by which the metals are set free, being different for each group.

(To be continued).

Chemical Society.—An Extra Meeting will be held on Thursday, June 13th, at 8.30 p.m., when Professor J. B. Farmer, F.R.S., will deliver a discourse entitled "Some Borderline Problems in Botany."

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd instant, Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Commander G. R. Bethell, late R.N., and Dr. Hans Goldsmidt were elected Members. The Chairman reported the decease of Sir Benjamin Baker, K.C.B., a Manager, and a Resolution of Condolence with the relatives was passed. The Special Thanks of the Members were returned to Mr. Oswald Lewis for his donation of 5 guineas to the fund for the Promotion of Experimental Research at Low Temperatures.

THE RAPID DETERMINATION OF NICKEL IN STEEL.*

By Dr. GEORGE T. DOUGHERTY, Chicago, Ill.

(Concluded from p. 262).

Method for Cupriferous Nickel Steel.

A LARGE majority of pig irons and steels produced in the United States are practically free of copper. The main source of copper steels in circulation is Cornwall ores in the Lebanon, Pa., District, which yield pig irons running 0·75 to 1·25 per cent of copper. Copper, like nickel, reacts with potassium cyanide, and therefore if both copper and nickel are present in a steel, copper must be previously removed or allowed for. If we do not know beforehand the exact per cent of copper present and must separate it from nickel we will start by treating 1 grm. of steel with 20 cc. hydrochloric acid (1·10 sp. gr.) When action ceases flocks of insoluble carbide of nickel will be seen floating in the solution. Add 2½ cc. nitric acid (sp. gr. 1·20) and boil one minute to decompose nickel carbide and oxidise the iron. Proceed further, as described in the above method, for copper-free nickel steel to the point of filtering after precipitating with ammonia and diluting to 500 cc. If copper is absent or is present only in small quantity the ammoniacal filtrate will be very faintly bluish or greenish from the presence of nickel, but if 1 per cent of copper is present in the sample the ammoniacal filtrate will be pretty plainly blue. One per cent of copper makes a far stronger blue colour with ammonia than 3½ per cent of nickel does. Now take 250 cc. of the filtrate; add 25 cc. hydrochloric or just enough to acidify it, and then 14 cc. more, so that the liquid will contain 5 per cent of free hydrochloric acid, and then be sufficiently acid when sulphuretted hydrogen gas is subsequently passed into it to precipitate copper free of any nickel. An apparently trifling precipitate of copper sulphide may amount to notable figures, and therefore must be filtered off and washed with water containing some sulphuretted hydrogen. The filtrate is next boiled and oxidised if necessary with a little potassium chlorate to clear up. Add ammonia to neutralise, not over 1 cc. in excess. Cool and titrate.

Solutions Required.

Ammonium Chloride Solution.—Use 555 grms. of the salt in 2 litres of water. If there is any sediment, filter. The salt dissolves readily without any application of heat if the bottle is shaken vigorously. It is often more convenient to make it up by mixing hydrochloric acid and ammonia, as described elsewhere in this article. Of ammonium chloride solution 270 cc. is needed for each analysis, taking 1 grm. of steel.

Standard Nickel Solution.—Dissolve 2·0040 grms. of Merck's "highest purity" nickel in nitric acid and dilute to 2 litres. Each cubic centimetre equals 0·001 grm. nickel. In lieu of Merck's nickel Orford Copper Company's commercial nickel may be used, on the basis of being 99 to 99½ per cent, say 99·25 per cent.

Standard Potassium Cyanide Solution.—Use 24 grms. in 2 litres. It changes slowly and appreciably, and must be re-standardised every two or three days for particular work. For standardisation, take 50 cc. of the standard nickel solution (equals 0·050 grm. nickel) with a pipette; let it run into a No. 4 Griffin beaker; add 100 cc. water, 50 to 80 cc. hydrochloric acid; throw a bit of litmus paper; add nearly as much ammonia as you have added hydrochloric acid and then more, until the litmus paper has turned blue; add a little hydrochloric acid to acidify, and again, but very cautiously, ammonia, ½ to 1 cc. at a time, until the colour of the solution has become bluish or the litmus paper has turned blue, not over 1 cc. in excess. Throw out the litmus paper after rinsing it slightly. Cool.

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* From the *Iron Age*, April 25, 1907.

Add 5 cc. of silver nitrate solution and 5 cc. of potassium iodide solution, whereupon a white opacity or cloudiness will develop in the liquid. Run the potassium cyanide in from a burette and toward the end move cautiously, one drop at a time, with good stirring until the very last drop suddenly clears up the whole liquid. Deduct 0·2 cc. from the burette reading for a blank correction, and by the remainder divide 0·050 grm. nickel. One cubic centimetre of the freshly made potassium cyanide solution is equivalent to about 0·002500 grm. nickel.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

The plans for the restoration of the main building of this College have now been approved by the Society of Merchant Venturers; they involve very considerable changes in the arrangements of the original building.

In the basement the engineering workshop and forge will still be located; as also the electrical engineering laboratory and the hydraulic laboratory, both of which will, however, be much larger. A large special shed for motor car engineering will be provided, and it is hoped that the provision of a special department of this kind will not only be useful to young men in the city and West of England, who desire to enter this promising branch of engineering, but that it may also tend to a great development of the motor car industry in the city itself. A portion of the space at the back of the College will be covered over, and in it will be placed the experimental engine, dynamos, and central electric light and power station, now situated in the Rosemary Street branch building of the College, as well as the testing machines of various kinds. On this floor also will be found the rooms of the Professors of Electrical Engineering and Motor Car Engineering, the boiler house, heating chamber, battery house, and the head porter's lodge.

On the ground floor the Great Hall will be retained in its original position, and here also will be the rooms for the Governors, Principal, Registrar, Clerks, and Professor of Mathematics, together with three ordinary class-rooms, a lecturer's common room, a large common room for male students, and the head porter's house.

On the first floor will be found the gallery of the Great Hall, a large mechanical laboratory, engineering lecture room, drawing office, refectory, and a woman's common room, as well as a room for the Professor of Mechanical Engineering, cloak-rooms, &c.

The second floor will include the lesser hall, physical laboratory, optical laboratory, photographic laboratory, physical lecture theatre, two science lecture rooms, two ordinary class-rooms, library, research laboratory, &c., while on the new third floor provision is made for a gymnasium with dressing room, lavatories, &c., attached, and for the chemical department, which will include a chemical lecture theatre, preparation room, elementary chemical laboratory, advanced chemical laboratory, balance room, combustion room, Professor's room, and stores. The fume closets will be built outside the main laboratories, so will also the store for dangerous chemicals.

It is confidently expected that the whole of the work of restoring and refitting the building will be completed in time for the students to return to the main building in September, 1908. From the description of the provision to be made, it will be seen that the Governors are concentrating the work of their College so as to provide a much more extensive equipment for those departments which train civil, mechanical, electrical, mining, and motor car engineers, and which prepare for the B.Sc. degrees of the University of London in Science and Engineering. With this end in view they will discontinue certain portions of the work formerly undertaken by the College.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part II.—Analysis of the Silver, Copper, and Tin Groups.

By Arthur A. Noyes and William C. Bray.

(Continued from p. 260).

Test Analyses.

Numerous analyses were made to test the efficiency of the process above described. Nearly all of those which were made after the procedure assumed final form are reproduced in the tables below. In these tables the numbers in each vertical column show the weights in milligrms. of the various elements which the solution submitted to analysis contained. The results of the tests for each element are shown by the letters following these numbers. That the result was satisfactory is indicated by the letter S; that is, when the element was present, that the test for it, however small, was unmistakable, and therefore conclusive, and when the element was absent that a good blank test was obtained. When the test was very small, especially in comparison to the quantity of the element present, though still unmistakable, this is sometimes indicated by the symbol S—. When in the presence of the element the test failed, or in its absence a result was obtained that might be thought to indicate its presence, the letter F is used. When the result was doubtful or inconclusive, owing to the appearance or small size of the precipitate, this is indicated by the letter D. When the test was not tried, if the element was present, a dash is used in place of a letter; or, if the element was not present, dots are inserted.

Silver Group.

All these analyses (Nos. 1—9) were begun at P. 11 and carried through P. 15.

T.A. No.	1	2	3	4
Pb	500 S	500	..	..
Ag	0 S	1 S	500 S	500 S
Hg	0 S	1 S	0 S	1 S

T.A. No.	5, 6	7	8	9
Pb	..	..	..	..
Ag	0 S	1 F	1 S—	2 S
Hg	500 S	500 S	500 S	500 S

Copper Group.

Analyses Nos. 10—20 were begun at P. 21 and were carried through P. 23—30, P. 22 being omitted. In addition, tin was tested for by P. 25, 41, 42, 45, and 47.

T.A. No.	10	11	12	13
Hg . ..	500 S	500 S	500 S	500 S
Sn (ous) .	0 S	2 F	4 S	2 S—, F (*a*)
Pb	0 S	1 S—	1 F	2 S
Bi	0 S	1 S	1 S	0 S
Cu	0 S	1 S	1 S	0 S
Cd	0 S	1 S	1 S	0 D (*b*)

T.A No.	14	15	16	17
Hg . ..	1 S—	0 S	0 S	1 S
Sn (ous) .	2 S—, F (*a*)	0 S	0 S	2 S
Pb . ..	1 S	0 S	0 S	1 S
Bi	500 S	500 S	0 S	1 S
Cu . ..	1 S	0 S	500 S	500 S
Cd . ..	1 S	0 S	0 D (*b*)	1 S

T.A. No.	18	19	20
Hg	0 S	1 S	2 S
Sn (ous)	0 S	2 S	0 S
Pb	0 S	1 F	1 S
Bi	0 S	1 S	1 S
Cu	0 S	1 S	1 S
Cd	500 S	500 S	500 S

* From the *Technology Quarterly*, xix., No. 3, September, 1906.

Analyses Nos. 21—28 were begun at P. 21, the H_2S precipitate was digested once with 10 cc. ammonium polysulphide (P. 22), and the residue analysed by P. 23—30.

T.A. No.	21	22	23	24
Hg (ic)	2 S	1 D	..	..
Cu	..	..	2 S— (*c*)	5 S
Bi	..	..	..	..
Sn (ous)	..	..	300 S	300
Sb (ous)	300 S	300 S	..	..

Ta No.	25	26	27	28
Hg (ic)	..	..	..	..
Cu	3 S	2 S	2 S (*c*)	3 S
Bi	..	500 S	..	..
Sn (ous)	300	..	50 S	..
Sb (ous)	..	..	..	200 S

Analyses Nos. 29 and 30 were made in the same way, except that 25 cc. ammonium monosulphide was used.

T.A. No.	29	20
Hg (ic)	1 S	1 S
Cu	1 S (*c*)	1 F
Sb (ic)	300 —	..
As	..	250 —
Sn (ic)	..	250 —

Tin Group.

In analyses Nos. 31—56 the substances were dissolved directly in ammonium polysulphide and the solution treated by P. 41—47.

T.A. No.	31	32, 33	34, 35, 36	37, 38	39, 40	41, 42, 43
As	0 S	2 S	1 S	500 S	..	..
Sb	500 S	500 S	500 S	0 S	0 S	1 S
Sn	..	..	..	0 S	500 S	500 S

T.A. No.	44, 45	46	47	48	49	50
As	..	..	..	0 S	1 S	..
Sb	500 S	500 S	500 S	0 S	1 S	1 S
Sn	0 S	1 S—(*f*)	1 S	500 S	500 S	1 S

T.A. No.	51	52	53, 54	55	56
As	2 S	1 S	500 S	500 S	500 S
Sb	2 S	200 S	1 S	1 S	0 S
Sn	2 S	500 S	1 S	1 S—, F (*a*)	1 S

In experiments Nos. 57—90, in which a large quantity of an element of the copper group was present with the tin group, the analysis was begun at P. 21, the H_2S precipitate was treated once with 10 cc. ammonium polysulphide, and the solution analysed by P. 41—47. The copper group residue was not treated by P. 23—25 to recover tin.

T.A. No.	57	58	59	60	61	62
Bi	500 —	500 —	500 —	500 —	500 —	500 —
As	0 S (*g*)	1 F	2 S	1 S	..	..
Sb (ous)	0 S	1 S	2 S	0 S	..	..
Sn (ous)	0 S	1 F	2 S	0 S	2 S	1 S (*h*)

T.A. No.	63	64	65	66	67	68
Hg	500	500 —	500 —	500 —	500 —	500 —
As	0 S (*g*)	1 S	2 S	0 —	..	..
Sb (ous)	0 S	1 S	2 S	0 S	..	..
Sn (ic)	0 S	1 F	2 F	5 F	5 F	10 S (*i*)

T.A. No.	69	70	71	72
Cu	500 —	500 —	500 —	500 —
As	0 S (*g*)	1 S	2 S	0 S
Sb (ous)	0 S	1 S	2 S	0 S
Sn (ous)	0 S	1 F	2 F	2 F

T.A. No.	73	74	75
Cu	500 —	500 —	500 —
As	..	..	..
Sb (ous)	..	..	..
Sn (ous)	4 S—, F (*a*)	5 S (*i*)	3 S—, F (*a*) (stannic)

T.A. No.	76	77	78	79, 80	81
Cd	500 —	500 —	500 —	500 —	500 —
As	0 S	2 S	1 S	1 S	0 S
Sb (ous)	0 S	2 S	1 S	1 S	0 S
Sn (ous)	0 S	2 F	0 S	2 F	10 F
Sn (ic)	0 S	..	..	..	..

T.A. No.	82	83	84	85
Cd	500 —	500 —	500 —	500 —
As	..	..	..	..
Sb (ous)	..	..	..	..
Sn (ous)	10 S—, F (*a*)	15 S (*h*)	15 S—, F (*a*)	20 S (*i*)
Sn (ic)	..	..	..	..

T.A. No.	86	87, 88	89	90
Cd	500 —	500 —	500 —	500 —
As	..	..	..	..
Sb (ous)	..	..	..	..
Sn (ous)	25 S—, F (*a*)	25 S	..	..
Sn (ic)	..	..	3 F	5 S (*i*)

Analyses Nos. 91—97 were made by Mr. A. L. Smith in the same way as the preceding ones, except that 25 cc. ammonium monosulphide, instead of 10 cc. polysulphide, were used in digesting the H_2S precipitate.

T.A. No.	91	92	93	94
Hg (ic)	..	..	..	..
Bi	500 —	500 —	..	..
Cd	..	..	..	500 —
Cu	..	..	500 —	..
As (ic)	..	..	..	..
Sb (ic)	2 S	4 S	2 S	2 S
Sn (ic)	5 F (*m*)	10 F (*m*)	5 S	5 S

T.A. No.	95	96	97
Hg (ic)	..	..	500 —
Bi	500 —	..	..
Cd	..	250 —	..
Cu	..	250 —	..
As (ic)	..	..	1 S
Sb (ic)	1 S	1 S	1 S
Sn (ic)	5 F (*m*)	5 F (*m*)	5 F (*m*, *n*)

In analyses Nos. 98—100, also made by Mr. A. L. Smith, the solution in ammonium monosulphide and the residue were treated separately in order to detect tin. It was not detected in any case in the analysis of the solution. The results shown in the table were obtained in the analysis of the residue.

T.A. No.	98	99	100
Hg (ic)	250 —	250 —	..
Bi	250 —	250 —	..
Cd	..	..	250 —
Cu	..	..	250 —
Sn (ic)	2 F	5 S	3 S—, F (*a*)

Mixtures containing the Rarer Elements.

Analyses Nos. 101—105 were made, starting at P. 41, with an ammonium polysulphide solution, and following P. 42, 43, and *P. 43*a*—43*e*.

T.A. No.	101	102	103	104	105
As	..	..	300 S	200 S	200 S
Sb	..	..	200 —	..	..
Sn	..	..	200 —	200 —	200 —
Se	0 S	1 S	1 S	1 S	0·5 S
Te	0 S	1 S	1 —	2 S	1 S
Mo	100 S	50 S	1 S	0 S	0·5 S

Analyses Nos. 106—108 were begun at P. 21, the H_2S precipitate was extracted with ammonium polysulphide (P. 22), the solution was analysed by P. 41—43 and *P. 43*a*—43*e*, and the residue treated by P. 23, 24, and *P. 24*a*.

T.A. No.	106	107	108
Cu..	300 —	200 —	100 —
Hg	0 S	0 S	0 S
Pt	5 S (*l*)	3 S (*k*)	2 S (*k*)
Au	5 S (*k*)	3 S (*k*)	1 S (*l*)
Te..	..	..	10 S

Analyses Nos. 109—111 were made by Mr. A. L. Smith, beginning with P. 21 and following through the whole process as described in P. 21—47. Ammonium monosulphide was used in separating the copper and tin groups.

T.A. No.	109	110	111	112 (*s*)	113
Hg (ic)	1 D (*o*)	1 —	1 F (*o*)	..	2 D (*o*)
Pb ..	1 F	1 S	1 S—	..	1 S
Bi ..	0 S	1 S (*t*)	1 S (*t*)	..	1 S
Cd ..	1 D	1	1 F (*q*)	1 S	2 S
Cu ..	1 S	1 S	1 S	..	1 S
As (ic).	1 F	1 S	1 S	..	1 S
Sb (ic).	0 S	1 S	1 S—	1 S	1 S
Sn (ic).	2 S	1 S—, F (*a*)	1 S—, F (*a*)	..	2 S
Pt ..	1 S (*f*)	1 S (*u*)	1 S	..	1 S (*f*)
Au ..	1 S (*f*)	1 S (*u*)	1 S (*f*)	..	1 S (*f*)
Se ..	1 F	1 F (*x*)	1 S—	1 S	2 F (*x*)
Te ..	1 F	1 F	1 S— (*r*)	1 S	2 F (*y*)
Mo ..	1 D	1 D	1 S— (*r*)	1 S	2 S

The test analyses of the silver group (Nos. 1—9) show that 1 mgrm. of mercurous mercury is detected in the presence of 500 mgrms. of either lead or silver; and that 1 mgrm. of silver is detected without difficulty in the presence of 500 mgrms. of lead, but that in the presence of 500 mgrms, of mercury 1 mgrm. of silver lies at about the limit of detectability.

The test analyses of the copper group (Nos. 10—20) show—at any rate when the ammonium sulphide treatment is omitted—that even 1 mgrm. of mercury, bismuth, copper, or cadmium is detected in the presence of 500 mgrms. of any other one of these elements; that with lead in presence of 500 mgrms. of any one of these elements 1 mgrm. is near the limit, probably owing to the difficulty of securing complete precipitation with H_2S; and that with stannous tin the limit of detectability is at 2 mgrms. The blank tests were satisfactory in all cases, except that a very small dark precipitate was sometimes obtained in the cadmium test with H_2S. Even when the H_2S precipitate was treated with ammonium polysulphide (T.A. Nos. 21—28), which dissolves some copper and mercury, these elements were detected in all cases where 2 mgrms. were present; and when monosulphide was used (as in T.A. Nos. 29 and 30) 1 mgrm. of mercury was twice detected, while with copper it was found in one analysis and lost in the other.

The test analyses of the tin group in which the copper group was not present, which were begun with an ammonium polysulphide solution of the elements (Nos. 31—56), show that 1 mgrm. of arsenic, antimony, or tin is invariably detected, even in the presence of 500 mgrms. of any other one of these elements.

The test analyses in which the elements of the tin group were associated with 500 mgrms. of an element of the copper group, and in which the H_2S precipitate was treated with ammonium polysulphide (Nos. 57—90), show that 1 mgrm. of arsenic or antimony is almost always detected; but that a much larger quantity of tin in some combinations is not detected if only the ammonium sulphide solution is analysed for it. Thus, while in the presence of bismuth 1 to 2 mgrms. of stannous tin were found, yet in the presence of copper 4 to 5 mgrms., and in that of cadmium 10 to 15 mgrms. of it were lost; and 3 to 5 mgrms. of stannic tin were lost in the presence of mercury or cadmium.

In the analyses in which ammonium monosulphide was used (Nos. 91—97), the detection of antimony in the higher state of oxidation and of arsenic is nearly as satisfactory, 1 or 2 mgrms. having been always found; but a larger quantity of stannic tin remains with the copper group than when the polysulphide is used, 5 mgrms. being retained even by bismuth.

These results clearly show the necessity of testing for tin in the analysis of the copper as well as of the tin group, and T.A. Nos. 98—100 show that it can be detected in the copper group analyses when 3 mgrms. are present.

In the test analyses with mixtures containing the rarer elements (Nos. 101—113) 1 mgrm. of platinum or gold was always detected; and the same was true of 1 mgrm. of selenium, tellurium, and molybdenum in the analyses that started at the beginning of the tin group, but not in those where elements of the copper group were present and the analysis was begun with the H_2S precipitation.

Notes to the Tables.

(*a*) The confirmatory test with $HgCl_2$ failed, but a distinct precipitate of SnS_2 was obtained.

(*b*) A very small dark precipitate was obtained.

(*c*) No blue colour was produced with NH_4OH, but a slight pink precipitate with $K_4Fe(CN)_6$ was visible on the filter.

(*d*) A good blue colour was obtained with NH_4OH, showing that a small quantity of copper is not dissolved out of a large copper group precipitate by the polysulphide.

(*e*) No blue colour could be seen, but a very distinct pink precipitate formed with $K_4Fe(CN)_6$.

(*f*) In this analysis the confirmatory tin test failed, but this was doubtless due to the fact that the SnS_2 precipitate was filtered off and dissolved in HCl, instead of evaporating the mixture as usual.

(*g*) The HCl precipitate from the polysulphide solution was very light coloured, or, if not, when it was extracted with NH_4OH the solution gave no precipitate with HCl, so the analysis was not carried further.

(*h*) A fair SnS_2 precipitate was produced, but owing to an accident the confirmatory test was not tried.

(*i*) The SnS_2 precipitate produced in P. 47 was estimated to contain only 1—3 mgrms. Sn.

(*k*) In these analyses the moist H_2S precipitate was left on the filter for several hours before treating with ammonium polysulphide.

(*l*) Satisfactory tests were obtained for gold and for platinum both in the copper and tin groups; and the final precipitates were not far from equal in size.

(*m*) No precipitate of SnS_2 was produced in p. 47.

(*n*) The residue undissolved by ammonium sulphide was treated by P. 23, 24, 25, 41, and 42, and the HCl solution so obtained reduced directly with Zn, the residue dissolved, and $HgCl_2$ added; but no test for tin was obtained.

(*o*) A black precipitate was produced in the test with $SnCl_2$, probably due to the presence of gold. It was treated with hot HNO_3 (1·20), and it did not dissolve, showing it was not wholly mercury; the solution, after evaporation with HCl, was tested with $SnCl_2$, but only an inconclusive turbidity was obtained.

(*f*) Tests for these elements were obtained in the analyses of both the copper and tin groups.

(*q*) All or nearly all the cadmium failed to be precipitated by H_2S from the 100 cc. of solution containing 4 cc. HCl (1·12), even though the gas was passed in for ten minutes, for it was recovered from the filtrate by adding 50 cc. more water and passing in H_2S for ten minutes, and then confirmed by P. 23, 27, and 30.

(*r*) Nearly all the tellurium and molybdenum failed to be precipitated by H_2S, for they were recovered from the filtrate by adding NH_4OH and NH_4SH and acidifying, and were detected by treating the precipitate by P. 43, *43*a*, *43*c*, *43*d*, and *43*e*.

(*s*) In T.A. No. 112 the last part of P. 43 and *P. 43*b* were omitted.

(*t*) No distinct turbidity was visible, but upon filtering and treating with sodium stannite the filter was much darkened.

(*u*) Tests for these elements were obtained only in the analysis of the tin group.

(*x*) A red precipitate separated in the lead test upon evaporating with H_2SO_4, which was probably selenium, and indicated that it had not been dissolved out by $(NH_4)_2S$.

(*y*) In testing for arsenic with $MgCl_2$ a flocculent precipitate accompanied the crystalline one of $MgNH_4AsO_4$, and on dissolving this in HCl and adding H_2S a black precipitate resulted. This was dissolved in HCl and $KClO_3$ and treated by *P. 24*a* ; a black precipitate resulted, showing that tellurium was precipitated with the arsenic.

(To be continued).

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, May 16th, 1907.

Prof. R. MELDOLA, F.R.S., Past President, in the Chair.

MR. E. GARDNER was formally admitted a Fellow of the Society.

It was announced that the following Address would be presented to the Société Chimique de France on the occasion of the celebration of its Jubilee.

Address from the Chemical Society to the Société Chimique de France.

The ties of sympathy connecting the Chemical Society of France and the Chemical Society resemble the bonds uniting members of the same family rather than those associating friends drawn together by mere community of interests.

On the occasion of our Jubilee celebration in 1891 your representative, M. Gautier, then President of the Société Chimique de Paris, reminded us that, prior to your foundation in 1857, M. Wurtz had paid a special visit to London in order to study the organisation of our Society, which had then been in existence for sixteen years, and further remarked "La Société Chimique de Londres été le modèle et la grande sœur de la Société Chimique de Paris."

It is now the privilege of the elder sister to send through her appointed delegates the congratulations of all English chemists to the Société Chimique de France on completing fifty years of active work in widening the boundaries of a science which has conferred such inestimable benefits on humanity.

How magnificent have been the contributions to knowledge made by your Society during those five decades is witnessed by your *Bulletin*, which in itself represents a historical survey of modern chemistry.

The satisfaction with which our Society embraces this opportunity of taking part in your *réunion* is not untinged by sadness, for we can no longer hope to meet amongst you two of the most illustrious of our *confrères*, whose loss your country, and, indeed, the whole world, have so recently had to deplore. This loss is felt all the more deeply by us since one of them was the doyen of our Honorary and Foreign Fellows.

In the genius of Marcellin Berthelot, the gifted founder of chemical synthesis and of thermo-chemistry, were united the savant and the statesman, a combination of qualities which must be rare in any age; whilst in Henri Moissan we mourn a colleague, the products of whose industry have been well described as taking a place amongst the greatest achievements in inorganic chemistry.

(Signed) WILLIAM RAMSAY, President.
ALEXANDER SCOTT, Treasurer.
M. O. FORSTER, ARTHUR W. CROSSLEY, } Honorary Secretaries.
HORACE T. BROWN, Foreign Secretary.

Certificates were ready for the first time in favour of Messrs. William Arthur Colebourne, 34, Camp Street, Broughton, Manchester; Robert Cornthwaite, Agricultural Laboratory, Halifax; Charles William Lamb Jensen, Oakhill, nr. Bath; Charles Horne Warner, 24, Gordon Street, Gordon Square, W.C.

A certificate has been authorised by the Council under By-law I. (Par. 3) in favour of Ruchi Ram Sahni, M.A., Government College, Lahore, India.

Of the following papers, those marked * were read:—

*100. "*The Relation between the Crystalline Form and the Chemical Constitution of Simple Inorganic Substances.*" By WILLIAM BARLOW and WILLIAM JACKSON POPE.

The authors pointed out that only two simple homogeneous close-packed assemblages of equal spheres exist; one of these possesses holohedral cubic symmetry, and the other holohedral hexagonal symmetry with the axial ratio, $a : c = 1 : 0{\cdot}8165$. They showed that close-packed homogeneous assemblages made up of two or more kinds of spheres of nearly the same size must approximate in marshalling to one or other of the above types of assemblage or some homogeneous combination of these. All the known crystalline forms exhibited by the elements can be interpreted in the light of the above geometrical principles; the latter also explain how binary compounds composed of two elements of the same valency, such as the alkali halogen compounds, crystallise in the cubic system, and how silver iodide, which crystallises in the hexagonal system, exhibits the axial ratio, $a : c = 1 : 0{\cdot}8196$.

An examination of the isomorphous series of tri-halogen compounds, to which the compounds CsI_3 and RbI_3 belong, shows that the axial ratios of these orthorhombic substances are also in accordance with the geometrical principles stated above.

Descriptions were given of the homogeneous assemblages corresponding to the above substances and to the ammonium salts isomorphously related to certain of them. The crystalline forms of certain of the chlorates, carbonates, and nitrates were also discussed.

DISCUSSION.

Dr. DIVERS pointed out that, for the purposes of the authors, it was surely unnecessary, and, as introducing complexity, undesirable to do more than equalise the axial ratios of similar crystals by applying the law of the rationality of the axes. When the authors went on to multiply the equalised ratios by the factor, $\sqrt[3]{W/ac}$, and entitled the results "equivalence parameters," they served no useful end, since no further "equivalence" could be conferred upon ratios (or anything else, except their more complex expression) by multiplying them by this or any other factor.

He feared that the authors were risking failure to convince many chemists of the sufficiency of the assumption of their "valency volumes" to correlate chemical with crystalline structure, by demanding for the purpose of appropriate close packing that considerable deviations from simply proportioned volumes must be allowed them; for example, that volumes of a given valency are not quite equal, even under similar conditions, when they are of different chemical elements; and that, under different conditions, these volumes may vary considerably, even when of the same element; and that, also for close packing along with perservation of mechanico-chemical structure, the valencies must be, sometimes, exceptionally chosen; that, for

example, the alkali metals are to be univalent in their trihalides; sulphur bivalent in sulphates; nitrogen, tervalent in nitrates, and oxygen in hydroxyl compounds, sometimes of no valency.

What seemed to him to be, also, a serious objection to the packing of atoms to represent chemical constitution was that juxtaposition of atoms expressed chemical union in some cases and not in others. He also doubted whether with close packing and pressing out all interspaces the appropriate distances between the centres of the spheres, shown undeformed in the models and diagrams, would be sufficiently preserved. But, without the experience of the authors, that was too difficult a point for others to deal with adequately.

Dr. Tutton said he was glad that Prof. Pope in his exposition of the authors' paper had removed the doubt which had been created by their first paper as to the light in which they regarded the use of topic axial ratios. It was now made clear that their equivalence parameters were intended to supplement, for unrelated or only morphotropically related substances, the teaching of topic axial ratios with respect to the strictly related members of isomorphous series, and that the value of the topic axial ratios for expressing the structural relationships of the members of such series was undoubted by them. He pointed out that these ratios depended solely on constants determinable with the highest experimental accuracy, namely, the crystallographic axial ratios, the molecular weight, and the specific gravity, and that whilst the molecular volume represented the total relative change of volume on passing from one member to another, the topic axial ratios gave the actual changes in the separation of the structural units, the chemical molecules, in the three directions of space. The equivalence parameters of the authors suffered from an apparent want of such precision, essentially so from the different nature of the problem, and Dr. Divers had seized on this apparent weak point. He (Dr. Tutton) felt sure, however, having now had time to consider the previous paper of the authors and having seen the present one by their courtesy, that they would be able fully to justify their position, and that they were on the right track. He believed that the topic axial ratios and the equivalence parameters would together afford a complete account of the relationship between crystalline structure and chemical constitution, and it was pleasant to think that the papers introducing both had been communicated to this Society.

*101. "*Experimental Investigation into the Process of Dyeing.*" By Julius Hübner.

The author has examined quantitatively the absorption of basic, acid, and direct dyeing colouring matters by cotton, wool, silk, and other fibrous materials at different temperatures, with and without the addition of other substances to the dye-bath.

Parallel series of measurements were made on the absorption of the several classes of colouring matters by charcoal, graphite, China clay, and lampblack, and the following conclusions were established from the comparison.

Fibres of animal origin behave towards colouring matters in the main like charcoal, whilst cotton behaves similarly to graphite.

Thus, both cotton or graphite are practically unaffected by acid dye-stuffs, either hot or cold, whilst wool or charcoal absorb the colouring matter freely.

The parallel behaviour of cotton and graphite, and of wool and charcoal is also illustrated by the effect of acids, sodium sulphate, &c., added to the dye-bath in the case of both acid and direct dyeing colouring matters. Similar analogies of behaviour are observed in the absorption of basic colours by the materials mentioned.

The relative absorptions were determined at different temperatures.

Discussion.

Dr. Divers pointed out the importance of this work as showing that dyeing was not of a chemical, but of a physical, nature. The fact that absorption by charcoal was of the same order of things as absorption of colours by fibres was of much interest.

Mr. Grant Hooper said that in the brief *résumé* of the paper which the author had given the conclusions had not been stated, and he asked whether the increased amount of colouring matter taken up by disintegrated cotton as compared with the unbroken fibre was not explained by the fact that the colour more easily gained access to the interior of the fibre when the latter was torn. He suggested that the imbricated structure of wool probably facilitated the access of dye substance to the interior of tha fibre, and so accounted in a similar manner for the comparative readiness with which wool also took up colouring matter.

He further asked whether, in view of such apparent action and of the results obtained in the experiments with fibrous material on the one hand, and charcoal and inorganic substances on the other, the conclusion was drawn that the dye was retained by a process of adsorption.

Dr. Feilmann remarked that Suida had also published extensive accounts of experiments on the dyeing of mineral substances, &c., some two years or more ago, and that Suida's results seem to show that a kind of double decomposition occurred, so that the process was of a more or less chemical character, whereas Mr. Hübner's experiments, on the other hand, tended rather to show that the process was mainly physical, depending on absorption.

102. "*Esterification Constants of Substituted Acrylic Acids.*" (Part II.). By John Joseph Sudborough and Ebenezer Rees Thomas.

As an extension of the work already published (*Trans.*, 1905, lxxxvii., 1840), the authors have determined the esterification constants of a number of unsaturated acids with methyl alcohol at 15°. The acids experimented with were cinnamic, phenyl*iso*crotonic, β-ethylacrylic, ethylidenepropionic, and allylacetic. The results indicate in a decisive manner the retarding effect which a double bond in the $\alpha\beta$-position has on the velocity of esterification. The constants for phenyl*iso*crotonic and cinnamic acid are in the ratio 74 : 1, and of the β-ethylacrylic, ethylidenepropionic, and allylacetic acids in the ratio 1 : 50 : 26·7.

103. "*The Addition of Bromine to the α- and β-Chloro- and Bromo cinnamic Acids and their Methyl Esters.*" By John Joseph Sudborough and Gwilym Williams.

The products obtained by the addition of bromine to the α- and β-bromo- and chloro-cinnamic acids and their methyl esters have been examined in order to determine whether in each case the α- or β-compound and the stereoisomeric *allo*-compound yield the same dibromide.

The addition of bromine to the α-compounds does not take place readily in the dark. In daylight both α-bromo-acids yield the same *ααβ-tribromo-β-phenylpropionic acid*, m. p. 151—152°. The corresponding *methyl ester* melts at 47—48°. The two β-bromo-acids combine with bromine, both in the dark and in light, yielding the same *αββ-tribromo-β-phenylpropionic acid*, m. p. 146—147°. The corresponding *methyl ester* melts at 42—43° (decomp.). The α-chloro-acids do not combine with bromine in the dark, and in daylight each yields a mixture of two dibromides, which, so far, have not been separated.

The two β-chloro-acids combine more readily with bromine, yielding the same *β-chloro-αβ-dibromo-β-phenylpropionic acid*, m. p. 143—144° (decomp.).

104. "*The Addition of Bromine to Unsaturated Compounds.*" (Part I.) By John Joseph Sudborough and John Thomas.

The work, of which a preliminary note has already appeared (*Proc.*, 1906, xxii., 318), has been continued. The rate of addition of bromine to various olefine acids has been determined at 15° in carbon tetrachloride solution. The accelerative effect of sunlight has been confirmed. Of the following acids examined, cinnamic, crotonic, phenyl*iso*crotonic, undecylenic, oleic, elaidic, erucic, brassidic, β-ethylacrylic, ethylidenepropionic, and allylacetic acids, all those containing the double linking in the

$\alpha\beta$-position unite with bromine but slowly in the dark, whereas all the other acids absorb bromine with great readiness under the same conditions, the reaction being practically complete in a few minutes.

The characteristic behaviour of the $\alpha\beta$-unsaturated acids may be used as the basis of a method for determining whether a double linking is in the $\alpha\beta$-position with respect to the carboxylic group or not.

103. "*Separation of Cadmium from Zinc as Sulphide in the presence of Trichloroacetic Acid.*" By John Jacob Fox.

A convenient method of separating cadmium from zinc as sulphide is furnished by the use of trichloroacetic acid. The quantity of trichloroacetic acid required is at least 10 grms. per 100 cc. of solution, but much greater concentrations can be used without affecting the precipitation of cadmium as sulphide. Even when the amount of the cadmium is small (5 mgrms. per 100 cc.), concentrations of trichloroacetic acid as great as 30 grms. of acid per 100 cc. do not prevent the whole of the cadmium being precipitated.

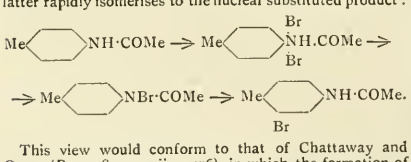
In this respect, trichloroacetic acid differs from both hydrochloric and sulphuric acids.

For the complete separation of cadmium and zinc, two precipitations are desirable; this is unnecessary, however, when the proportions of cadmium and zinc are about equal or when the cadmium is present in excess. If the presence of trichloroacetic acid is objectionable in the subsequent treatment of the solutions, a first partial separation of zinc and cadmium may be effected by the use of 1 grm. of hydrogen chloride per 100 cc. of solution.

106. "*The Mechanism of Bromination of Acylamino-compounds.*" (Preliminary Notice). By Julius Berend Cohen and William Ernest Cross.

In the ordinary process of brominating acylamino-compounds in acetic acid solution, the crystalline product which is first formed yields, on pouring it into water, the nuclear brominated compound. This intermediate compound has been isolated in the case of aceto-*p*-toluidide, and crystallises in brilliant yellow needles containing two atoms of bromine. It was very unstable in the dry state, slowly losing bromine, and changing into the original compound. The same result is more rapidly effected by shaking the ethereal solution with mercury or dry potassium carbonate. The ether then contains the unchanged aceto-*p*-toluidide. If, on the other hand, the bromine compound is poured into water or shaken with pyridine, &c., hydrogen bromide is at once eliminated, and a quantitative yield of 2-bromoaceto-*p*-toluidide is obtained.

The following provisional explanation is offered. An additive compound with one molecule of bromine is first formed, which in contact with water loses hydrogen bromide, and gives the nitrogen bromide compound. The latter rapidly isomerises to the nuclear substituted product:



This view would conform to that of Chattaway and Orton (*Ber.*, 1899, xxxii., 3576), in which the formation of the nitrogen bromide compound is found to precede the isomeric change from side-chain to nucleus. Up to the present, however, the authors have failed to obtain evidence of the presence of the nitrogen bromide compound.

107. "*Mixed Semi-ortho-oxalic Compounds.*" By George Druce Lander.

The amide chlorides of methyl and ethyl oxanilates are stable below 100°. On decomposition by heat they pass by loss of hydrogen chloride into the imide chlorides, which are further resolved into alkyl chloride, carbon monoxide, and phenylcyanate, thus:—

$$CO_2R{\cdot}CCl_2{\cdot}NHPh \rightarrow CO_2R{\cdot}CCl{:}NPh + HCl \rightarrow$$
$$\rightarrow O{:}C{:}NPh + RCl + CO.$$

With sodium alkyloxides the amide chlorides yield *triethyl anilido-semi-ortho-oxalate*, $CO_2Et{\cdot}C(OEt)_2{\cdot}NHPh$, m. p. 69—70·5°, b. p. 172—174°/12 mm., and *trimethyl anilido-semi-ortho-oxalate*, similarly constituted, and having m. p. 80—82°. b. p. 182°/20 mm.

When heated under atmospheric pressure these compounds yield *ethyl* iso*diphenyloxaluric ethyl ester*, $PhN{:}C(OEt){\cdot}NPh{\cdot}CO{\cdot}CO_2Et$, m. p. 101—104°, and the corresponding *methyl* iso-*ester*, m. p. 131—133° respectively. Both *iso*-esters on hydrolysis with hydrogen chloride give diphenylparabanic acid.

(To be continued).

NOTICES OF BOOKS.

Commercial Organic Analysis. By Alfred H. Allen, F.I.C., F.C.S. Third Edition. Vol. II., Part III. London: J. and A. Churchill. 1907.

Owing to the death in 1904 of the author of this treatise the revision of Volume II. has been completed by Mr. A. R. Tankard, F.C.S., to whose efficient hands the task was entrusted at the special request of the author. One portion of the book was prepared by Dr. Henry Leffmann, who revised and added to Volume I. and the other parts of Volume II. This volume treats of the acid derivatives of phenols, aromatic acids, resins, and essential oils, and the properties, use, and examination for adulterants of every substance of commercial or scientific interest, which is included in one or other of the above classes, are minutely described. Certain parts of the book have been fundamentally altered in accordance with the facts that have been brought to light by recent research, and every page has been carefully revised; no analytical chemist should consider his library complete till he has obtained a copy of the latest edition of this treatise.

A Handy Book for Brewers. By Herbert Edwards Wright, M.A. Third Edition. London: Crosby Lockwood and Son. 1907.

In the third edition of this useful text-book the author has introduced many improvements, while keeping the general arrangement of the text unaltered. Modern discoveries which have a bearing upon any question connected with brewing are fully discussed, the work of Buchner and others upon zymase in particular being very carefully summarised, while a synoptic table of the enzymes has been added. The parts of the book which deal with pure chemistry have been considerably enlarged, and the student of brewing may find that the mass of material put before him is somewhat bewildering in its detail. However, the laboratory work with which the practical brewer should make himself familiar is carefully described; a rather fuller account of the use of the polariscope and polarimeter might perhaps be given, although possibly enough is said to enable straightforward determinations to be carried out. The author has been very careful not to dogmatise more than is absolutely necessary when dealing with the many disputed questions which meet the scientific brewer at every turn, and he has produced a safe and trustworthy book for the use of brewing students.

Agglutinants of All Kinds for All Purposes. By H. C. Standage. London: Archibald Constable and Co., Ltd. 1907.

This book contains more than five hundred recipes for the

preparation of cements and agglutinants for the most varied purposes. In order to facilitate reference to the recipes they are arranged under the headings of the different trades, the greater number being included in the sections devoted to the building, paper, and textile industries. Most of the recipes have been carefully tested by the author, or, if this has been impossible, he has had satisfactory evidence that they are reliable for the specified purposes, and some of the miscellaneous information relating to the methods and the compositions employed by metal workers and scientific instrument makers might find useful application in the laboratory; thus, valuable suggestions are given for joining rubber-tubing and for soldering glass. The composition of solders of all kinds is shown in a tabulated statement, and the short notes which are added on the characteristic properties of the chief materials employed should enable adaptations of the recipes to be made to suit special requirements.

The Electrolytic Dissociation Theory. By Prof. R. Abegg, Ph.D. Authorised Translation by Carl L. von Ende, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

This discussion of the results of Arrhenius's fruitful theory of electrolytic dissociation by one of the most distinguished of his disciples is a brilliant piece of work, and although it contains comparatively little that is new to students of the great Swedish physicist's own writings, it presents facts and works out formulæ in a very striking and lucid manner. It was hardly to be expected, perhaps, that full justice would be done to the work of the opponents of the theory, although criticisms of it which seem to carry weight are briefly surveyed. Stress is laid upon deductions from the theory and problems for which it seems like to provide a solution, and the development of equilibrium relations among electrolytes is treated specially fully. The book is one which students of physical chemistry will find it profitable to study and thoroughly digest; and even if they have already made themselves acquainted with the outlines of the theory they will find that this masterly little work will put before them fresh aspects of the subject.

Technische Anwendungen der Physikalischen Chemie. ("Technical Applications of Physical Chemistry"). By Dr. Kurt Arndt. Berlin: Mayer and Müller. 1907.

The technical applications of the most important results which have been obtained owing to the activity of investigators of the laws of physical chemistry are discussed in this book from an elementary point of view. Since there are many text-books dealing with technical electrochemistry the author has touched upon this branch only very lightly, and, on the other hand, devotes much space to the subjects of solution and catalysis. The measurement of high temperatures and the construction of various types of pyrometers are considered in detail, and in all cases the processes employed commercially are described more fully than the laboratory experiments upon which they were based; students in technical schools and colleges, however, who have some knowledge of theoretical physical chemistry will find that the book provides for them an admirable account of the more important applications.

Fuel, Water, and Gas Analysis for Steam Users. By John B. C. Kershaw, F.I.C. London: Archibald Constable and Co., Ltd. 1907.

The time must surely be at hand when the steady flow of books of this nature will begin to show signs of abatement—books that are excellent in themselves, and are apparently generally appreciated, but are written for a class that should not exist, namely, those who with quite insufficient scientific training undertake the work of skilled chemists, upon whom they often bring discredit by their incapacity. The engineer or steam user who requires directions for using a chemical balance will, it is hoped, soon be extinct, but in the meantime one who requires instruction of this nature cannot do better than to get this book. Although much of the analytical work is described in a very condensed form, which might lay pitfalls for the uninitiated, the value of the book is not inconsiderable in that it discusses in a broad spirit the practical applications of the test results, and emphasises the importance of the regular testing of materials, showing how the facts thus brought to light may be the means of decreasing expenditure or increasing efficiency. The work will, no doubt, meet with the approbation of steam users, and will give them some insight into analytical methods; it has been carefully written and well printed, although we notice a very misleading illustration of a burette reading on p. 75, the true value differing from that indicated by 0·02 cc.

Die Physik Roger Bacos. ("The Physics of Roger Bacon"). By Sebastian Vogl. Erlangen: Junge und Sohn. 1906.

This reprint of the author's inaugural dissertation for the doctorate contains a concise account of Roger Bacon's work on physical subjects, besides a short biography in which are related the main facts known about his life. The discussion of the authorities from whom he acquired his knowledge of physical phenomena includes brief notices of the early philosophers of Greece, Italy, and Arabia, and the writings of Bacon are quoted freely in order to illustrate as clearly as possible the originality and critical faculties he brought to bear upon the various questions which he investigated; it is shown that, although much of his work was of the nature of a compilation, the thirteenth century compiler was surrounded by difficulties with which his brother of the twentieth century does not have to contend. The chemical work of Bacon and his extraordinary belief in the powers of the philosopher's stone are not discussed, but the pamphlet gives a careful and well planned account of his physical work, more especially in the region of optics.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 19, May 13, 1907.

Action of Fluorine on Selenium. Selenium Tetrafluoride.—Paul Lebeau.—By subjecting selenium to the action of fluorine in a glass apparatus, Prideaux obtained a gaseous compound which he thought was selenium hexafluoride, SeF_6, basing the formula upon the density and the physico-chemical relations with the hexafluorides of sulphur and tellurium. However, the readiness with which fluorine forms oxyfluorides in presence of glass led the author to repeat these experiments, using a metal apparatus instead of glass. The selenium was placed in a copper tube connected at one end with the fluorine apparatus and at the other with a system of condensers cooled by liquid air. By this method a very small quantity of gas was obtained, but a colourless fuming liquid collected in the copper tube. This liquid attacks glass energetically, boils at about 100°, and decomposes with water, giving a solution which contains selenious acid and hydrofluoric acid. The compound can thus be analysed by dissolving a known weight in water and determining the fluorine and selenium in the solution. The formula is thus

found to be SeF_4. Sulphur, arsenic, boron, silicon, and carbon are not attacked by the tetrafluoride at its boiling-point; phosphorus sets selenium free, and phosphorus pentafluoride is formed. Selenium tetrafluoride is decomposed by the alkali metals, and attacks mercury at the ordinary temperature. The gaseous compound described by Prideaux is no doubt an oxyfluoride of selenium.

Spontaneous Oxidation of Hydrate of Cobalt in an Alkaline Medium.—André Job.—Although cobaltous compounds do not as a rule readily yield the corresponding cobaltic compound, hydrate of cobalt undergoes a change in air, absorbing oxygen. If equal volumes of the following solutions are mixed—sodium tartrate (50 per cent), cobalt sulphate (30 per cent), and soda (30 per cent)—the cobalt hydrate which is precipitated rapidly dissolves, and a violet-pink liquid is obtained, which turns green when shaken up with air or oxygen. The author found that the amount of gaseous oxygen absorbed increases indefinitely, while that taken up by the cobalt is limited. Hence the organic medium must take part in the reaction, reducing the green compound and keeping one part of the cobalt in the dissolved state, so that it constantly oxidises and gives up oxygen. The addition of glycerin stops this action, and thus renders the green compound much more stable. When glycerin is added (half a volume to one volume of tartrate), the absorption of oxygen by the liquid attains a finite limit, this being raised by increasing the amount of alkali added to the cobalt. Volumetric analysis (by iron pyrophosphate) shows that one atom of oxygen is fixed by two atoms of cobalt, and thus the compound obtained has the formula Co_2O_3. But the volume of gas shows that two atoms of oxygen are absorbed. Hence the organic medium must take up oxygen thus:—$2CoO + O_2 = 2CoO_2$, $2CoO_2 + A = Co_2O_3 + AO$. The oxide CoO_2 has been prepared; and it is found, moreover, that when manganese is substituted for cobalt, the oxide MnO_2 is primarily formed and a manganic salt (Mn_2O_3) exists after the oxidation.

Silicates of Alumina and Lime.—O. Boudouard.—The study of the fusibility of alumino-calcic silicates shows that there are two culminating points in the surface of fusibility corresponding to the temperatures 1510° and 1500°; the composition of these silicates is $SiO_2.Al_2O_3.2CaO$ and $SiO_2.Al_2O_2.8CaO$. To determine whether the first is actually a compound, it was subjected to a microscopic study, and was also analysed chemically, and the agreement between the values calculated and found was so close that there can be no doubt that the compound $SiO_2.Al_2O_3.2CaO$ exists.

Constitution and Properties of Boron Steel.—Léon Guillet.—Already noticed.

Condensation of Oxalic Ethers with Tertiary Aromatic Amines.—A. Guyot.—At a low temperature, in presence of a small quantity of aluminium chloride, oxalic ethers condense with tertiary amines, thus—

$$CO_2R—CO_2R + C_6H_5—NR'_2 = \\ = ROH + R'_2N—C_6H_4—CO—CO_2R.$$

With more aluminium chloride, or at a high temperature, the equation is—

$$CO_2R—CO_2R + 2C_6H_5—NR'_2 = \\ = ROH + \begin{matrix} R'_2N—C_6H_4 \\ R'_2N—C_6H_4 \end{matrix} > COH—CO_2R.$$

At a still higher temperature, or in presence of a large excess of aluminium chloride, the ether of a hexamethyltriamidotriphenylacetic acid is obtained:—

$$CO_2R—CO_2R + 3C_6H_5—NR'_2 = \\ \begin{matrix} & & R'_2N—C_6H_4 \\ ROH + H_2O + & R'_2N—C_6H_4 & —C—CO_2R. \\ & & R'_2N—C_6H_4 \end{matrix}$$

The author finds that all amines and ethers he has investigated possess this property. With sulphuric acid these condensation products give quantitatively $R_2N—C_6H_4—COOH$, $R_2N—C_6H_4—CO—C_6H_4—NR_2$, and $(R_2N—C_6H_4)_2=C—OH$, which are the substances formed when phosgene gas reacts with tertiary aromatic amines, and which are of technical importance as derivatives of triphenylmethane.

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VOL. XCV., No. 2481.

ON THE

DISCHARGE OF NEGATIVE ELECTRICITY FROM HOT CALCIUM AND FROM LIME.*

By FRANK HORTON, D.Sc., B.A., Fellow of St. John's College, Cambridge.

THIS paper contains an account of some experiments in which the negative leak from hot calcium was compared with that from platinum and from lime under similar conditions. The experiments were conducted in an atmosphere of argon or helium at a few millimetres pressure. The method of experimenting was as follows:—The negative leak from a platinum strip, heated by an electric current, was first investigated. The temperature of the strip was indicated by a thermocouple of wires of platinum and platinum with 10 per cent of rhodium, and the leak was measured by a delicate d'Arsonval galvanometer. Without changing the apparatus, the cathode was covered with metallic calcium by sublimation from an electrically heated calcium wire situated in the discharge tube near to the cathode. The negative leak from the calcium-covered cathode was determined at different temperatures. Some pure oxygen was then let into the apparatus and the calcium on the cathode was oxidised to lime. The excess of oxygen was then removed and the negative leak again measured. Finally, hydrogen was let into the apparatus and the effect of this gas on the negative leak from lime was investigated.

The results contained in the paper may be summarised as follows:—

1. The experiments with a platinum cathode showed that the negative leak from platinum in helium or argon at low pressures is practically the same as in air or oxygen. The variation of the negative leak per square centimetre with the temperature of the cathode can be expressed by an equation of the form used by O. W. Richardson and by H. A. Wilson, viz., $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$, where x is the current in ampères, θ the absolute temperature, and Q and A are constants.

2. The negative leak from calcium is enormously greater than from platinum at the same temperature. As with platinum, the variation of the leak with temperature can be expressed by the above equation, but the values of the negative leaks from calcium at different temperatures do not so closely agree with the values calculated from the equation as in the case of platinum. This is probably due to the greater experimental difficulties attending the use of calcium.

3. On oxidising the calcium on the cathode to lime there is an enormous increase in the negative leak, the leak from a lime cathode at 950° C. being about the same as the leak from calcium at 1400° C. The variation of the negative leak from lime with the temperature is not constant, but slowly decreases with continued heating.

4. The negative leak from lime in hydrogen is much greater than that in air or helium.

Since calcium is a much more electro-positive metal than platinum, it was to be expected that the negative leak from calcium would be greater than that from platinum at the same temperature. It would also be expected that the negative leak from calcium would be greater than that from lime under similar conditions; for in the case of lime we should expect the presence in the molecule of the electro-negative atom of oxygen to act as an attracting force tending to retain the escaping corpuscle. The present experiments, however, show that the negative leak from lime is greater than that from calcium. It is interesting to note that the metallic oxides which give the largest emissions of negative corpuscles when heated are the alkaline earths, and it is these also which exhibit most strongly the property of glowing when heated to a high temperature. It is not improbable that there is some connection between these two phenomena.

* Abstract of a Paper read before the Royal Society, Jan. 31, 1907.

ON THE THERMO-CHEMISTRY OF FLAME SPECTRA AT HIGH TEMPERATURES.*

By W. N. HARTLEY, F.R.S., D.Sc., Royal College of Science Dublin.

(Continued from p. 268).

PART II.—ON THE CHEMICAL REDUCTION OF THE ALKALINE EARTH SULPHATES.

FOR studying the action of gases in the flame on the insoluble sulphates, the minerals heavy spar, celestine, and selenite were chosen. Pieces of each measuring about 15 × 15 × 2 mm. were held by platinum forceps in the oxy-hydrogen flame for a definite period, and then dropped into a measured volume (50 cc.) of water. The unaltered mineral was insoluble in each case, but that which had undergone reduction, whether to oxide or sulphide, dissolved with a strongly alkaline reaction; the metal in solution was therefore determined volumetrically with standard acid. From the dissolved salts obtained from heavy spar, sulphuretted hydrogen was evolved in large quantity, somewhat less in the case of celestine, and hardly a trace with selenite. The following tabulated statement shows the results obtained:—

Anhydrous salt.	Time in flame.	Metal in solution.	Metal as sulphide.
	Minutes.	Grm.	
$CaSO_4$.. ..	15	0·0436	Practically none
$SrSO_4$.. ..	15	0·1150	10 per cent
$BaSO_4$.. ..	10	0·1055	Practically all
	15	0·1820	

If numbers be taken proportional to the above quantities, they are found to be approximately in the ratio of the atomic weights of the elements, thus:—

0·0436 grm. : 0·115 grm. : 0·182 grm. = 34 : 88 : 139
Ca : Sr : Ba = 40 : 87·5 : 137

A sample of celestine was heated in the flame for thirty-five minutes and dropped into water, acidified with acetic acid, and the sulphuretted hydrogen precipitated as lead sulphide, which was filtered off, converted into lead sulphate and weighed. The excess of lead was removed and the excess of strontium determined as carbonate.

Weight of lead sulphate.. ..	0·0314 grm.
Strontium as SrS	0·0091 ,,
Strontium carbonate	0·1718 ,,
Strontium as SrO	0·1022 ,,

These figures show that 8·1 per cent of the strontium in solution is in the state of sulphide.

The quantity of strontium reduced from sulphate in thirty-five minutes was 0·1022 grm., whereas that reduced in fifteen minutes was 0·115 grm., or the longer period in the flame has yielded the smaller product.

The Reduction of Barium Sulphate to Sulphide by Hydrogen.

A current of dry hydrogen was passed over a weighed quantity of precipitated dried barium sulphate heated to redness in a platinum tube. It was soon observed that sulphuretted hydrogen was evolved, probably according to the equations following:—

$$BaSO_4 + 4H_2 = BaS + 4H_2O \quad . \quad . \quad . \quad . \quad 1.$$
$$BaS + H_2O = BaO + H_2S \quad . \quad . \quad . \quad . \quad 2.$$

* A Paper read before the Royal Society, January 31st, 1907. (Revised March 22nd).

Sulphuretted hydrogen was still being evolved after a period of eight hours, when the experiment was stopped.

$BaSO_4$, initial weight ..	0·3226 grm.	= Ba 0·1897 grm.
$BaSO_4$, residue unchanged	0·0059 ,,	= Ba 0·0035 ,,
Diff., substance reduced .	0·3167 ,,	= Ba 0·1862 ,,
$PbSO_4$ from BaS, found .	0·2822 ,,	
Ba in BaS, found	0·1276 ,,	
Ba in BaO, found	0·0586 ,,	
Total Ba in $BaSO_4$ reduced	0·1862 ,,	

The reduced $BaSO_4$ is thus seen to have been composed of BaS = 0·1574 grm. and BaO = 0·0654 grm.; or about two-thirds sulphide and one-third oxide.

There can be no doubt that the initial action of the hydrogen is the reduction of the sulphate to sulphide, and that probably the whole of the sulphate is reduced; the secondary action, whereby the sulphide is converted into oxide with evolution of sulphuretted hydrogen, is slow and gradual with the barium compound, but takes place with greater facility with strontium, and with completeness in the case of calcium.

When heated to bright redness in a platinum tube through which a current of nitrogen and of carbon dioxide is passed, barium sulphate in neither instance undergoes any change.

When submitted to a white heat in a platinum tube at a reduced pressure for fifteen minutes, barium sulphate evolved no oxygen and the substance showed no alkalinity and was quite unchanged.

These experiments show that the hydrogen of the flame is the reducing agent by which the spectra are produced.

Part III.—The Thermo-chemistry of the Reduction Processes in Flame Reactions.

In studying the thermo-chemistry of flames, it is necessary to consider three separate questions:—

1. The effect on compounds of high temperatures solely.
2. The chemical action of other reacting substances in the flame gases on the compound in the flame.
3. The combined effect of high temperatures and reducing gases.

The thermo-chemical notation used is that of Dr. James H. Pollok (*Sci. Proc. Roy. Dublin Society*, 1899; *Trans. Chem. Soc.*, 1904, lxxxv., 603). The solid, liquid, gaseous, and dissolved states are indicated where necessary by a dot, dash, T, or circle (· — T o) placed below the formula of the substance. The heat evolved in the formation of a compound is indicated by ξ placed before its formula, which signifies *energy*.

The heat of a reaction is indicated by enclosing the equation in brackets and placing ξ before it. K° signifies a kilogrm. degree of heat or large calorie, *k°* similarly is a grm. degree of heat or small calorie. The chemical formula for a substance means, as is usual in this connection, its grm.-molecular weight.

(For the convenient symbol *g°* C., or grm.-degrees Celsius, instead of heat units or calories, and kilogrm. degrees of heat, K° C., we are indebted to Mr. J. Y. Buchanan, "On Steam and Brines," *Trans. Roy. Soc. Edin.*, 1894, xxxix., Part III., 529).

In discussing the process of hydrolysis of alkaline chlorides in the flame, we must take into account the following values and place the reaction at a temperature approaching 2000°, then—

$\xi HCl = 26$ K° and $\xi H_2O = 50{\cdot}6$ K°.

The heat of formation of solid potassium and sodium hydroxides is thus represented—

$$\xi(K + H + O = KOH) = 104{\cdot}6 \text{ K°};$$
$$\cdot \quad T \quad T \quad \cdot$$

similarly,—

$$\xi NaOH = 102{\cdot}7 \text{ K.}$$

The hydrolysis is then—

$$\xi(\underset{105{\cdot}7}{KCl} + \underset{50{\cdot}6}{H_2O} = \underset{104{\cdot}6}{KOH} + \underset{26}{HCl}) = -25{\cdot}7 \text{ K°}.$$

The corresponding value for NaOH is − 19·8 K°.

These reactions are not very strongly endothermic and therefore may occur and are reversible.

Among the common salts of lithium, the sulphate has the greatest stability, nevertheless in a gas flame it is reduced to oxide. Fused lithium sulphate was found to be a perfectly neutral substance, but when a bead of the salt had been heated in the flame of a Mecke burner for an hour it yielded a strongly alkaline solution which did not evolve sulphuretted hydrogen when acidified, nor did it effervesce. It therefore contained the oxide. On taking a larger mass and heating it on kyanite in the oxy-coal-gas blowpipe flame, care being taken that there should be no free carbon, the fused salt became reduced to sulphide. From this it appears that the normal process of reduction of the sulphates in the flame is that given in the two equations referring more particularly to barium sulphate. The difference in the heat of formation of lithium oxide and sulphide respectively, $\xi Li_2S = 115{\cdot}4$ K° and $\xi Li_2O = 141{\cdot}2$ K°; this shows how readily the former may be converted into the latter by the action of water-vapour, $\xi H_2O = 69$ K°, by reason of its being an exothermic action.

The flames from coal-gas, hydrogen, and carbon monoxide respectively, when burning in air, have a temperature as high as that of the melting-point of platinum, 1775° C. This temperature exceeds that of the metallurgical furnaces, in which sodium, potassium, cadmium, zinc, and magnesium are reduced and distilled on an industrial scale.

In the manufacture of sodium and potassium from the respective carbonates by means of carbon, the oxide is vaporised and chemically dissociated, thus $Na_2O = 2Na + O$, but the reaction is not reversible, owing to the presence of carbon, which immediately forms carbon monoxide with the oxygen, thus—

$\xi(C + O = CO) = 29{\cdot}4$ K° and $\xi(CO + O = CO_2) = 68{\cdot}3$ K°;

therefore, on the whole we have—

$$\xi CO_2 = 97{\cdot}4 \text{ K°}.$$

But—

$$\xi Na_2O = 100{\cdot}2 \text{ K°} \quad \text{and} \quad \xi K_2O = 98{\cdot}2 \text{ K°},$$

so that where the carbon is oxidised to carbon monoxide only, we have a considerable endothermic action, thus—

$\xi(Na_2O + C = CO + 2Na) = -71{\cdot}4$ K°, endothermic.

Although this equation does not take into account the fact that the Na_2O is already dissociated, this endothermic action may easily tend towards an exothermic character by the further combustion of the carbon monoxide to carbon dioxide, thus—

$$\xi(\underset{200{\cdot}4}{2Na_2O} + C = 4Na + \underset{97{\cdot}6}{CO_2}) = -102{\cdot}8 \text{ K°}, \quad \text{Endothermic}$$

or for one atom of oxygen − 51·4 K°.

If we suppose the operation to be a simple one of reduction, we have—

$$(\underset{270{\cdot}8}{Na_2CO_3} + 2C = 2Na + \underset{29{\cdot}4 \times 3}{3CO}) = -82{\cdot}6 \text{ K°}.$$

The reduction of K_2CO_3 in like manner would result in an endothermic value of − 90·6 K°. The same reasoning does not apply to lithium oxide, for all attempts to obtain lithium by a similar process of reduction have entirely failed. The reason is, that lithia more nearly resembles the alkaline earth oxides in its chemical properties; it is also the least volatile and least fusible of the alkali group; moreover, the energy required for its reduction is greater than that necessary for potassium or sodium. Thus,—

$\xi Li_2O = 141{\cdot}2$ K° and $\xi Na_2O = 100{\cdot}9$ K°.

An important fact may be observed here, namely, that whereas the banded spectrum of potassium is comparatively easy to obtain, that of lithium is very difficult, more diffi-

cult than that of sodium, and even the continuous rays are very weak. The same must be said of rubidium, with the additional remark that its band spectrum has never yet been seen. (A note appears on one of my photographs that there are just faint indications of bands in the strong continuous spectrum). This, undoubtedly, in part arises from the high value for the heat of formation of the oxides of these metals, and it is obvious that these particular properties of lithium serve to explain why the continuous glow observed by Lenard in the case of lithium is weaker than that of either sodium or potassium, which led him to remark that it was probably a property peculiar to that element. Even rubidium carbonate was reduced by mixing with carbon and heating to a particularly high temperature (Bunsen), but the greater volatility of rubidium compounds may facilitate their dissociation.

It is quite evident, then, that with the fusible and volatile oxides of sodium, potassium, and rubidium, reduction can be effected at a temperature not exceeding a white heat, and probably about 1400° C., certainly below the temperature of melting platinum, and below the highest temperatures of the coal-gas, the hydrogen, and the carbonic oxide flames.

Hence I conclude that the banded spectra of lithium, sodium, and potassium observed at the temperature of the oxyhydrogen flame are the spectra of the metals.

(To be continued).

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part II.—Analysis of the Silver, Copper, and Tin Groups.

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 272).

Confirmatory Experiments and References.

Analysis of the Silver Group.

P. 11, N. 1: *Solubility of* $PbCl_2$ *and* TlCl *in Water and in* HCl.—See Noyes (*Zeit. Phys. Chem.*, 1892, ix., 614, 623); Engel (*Ann. Chim. Phys.*, 1889, [6], xvii., 359); Ditte (*Comptes Rendus*, 1881, cxii., 718).

P. 13, N. 1: *Solubility of* $PbSO_4$.—See C. E., P. 26, N. 1.

*P. 13*a, N. 1: *Test for Thallium with* KI.—To 50 mgrms. Pb as $PbCl_2$, dissolved in 20 cc. water, 5 cc. H_2SO_4 (1·84) were added; the mixture was cooled and filtered, and to the filtrate a few drops KI solution were added; no precipitate appeared. The experiment was repeated, except that 1 mgrm. Tl as Tl_2SO_4 was also present; a pale yellow precipitate of TlI resulted.

To solutions containing 0·5 mgrm. Tl as Tl_2SO_4 and 4 cc. HCl (1·12), and 10 cc. or 20 cc. water respectively, a few drops of a normal KI solution were added; a yellow precipitate separated in the first experiment, but only a faint yellow turbidity appeared in the second.

*P. 13*a, N. 2: *Oxidation of Thallous Salts.*—100 mgrms. Tl as Tl_2SO_4 were dissolved in 10 cc HNO_3 (1·42) and evaporated to about 2 cc.; the solution was diluted to 20 cc., and 1 to 2 cc. HCl (1·12) added; a large light yellow precipitate separated, thus showing that some, but not much, of the thallium had been oxidised.

100 mgrms. Tl as Tl_2SO_4 were dissolved in 2 cc. HNO_3 (1·42), and about 5 cc. HCl (1·20) were added; a white precipitate separated at first, but dissolved on warming. The mixture was evaporated to about 2 cc., cooled, and diluted to 20 cc.; no precipitate separated, even when a little HCl was added, thus showing that the thallium was in the thallic state. The experiment was repeated, except that the aqua regia solution was evaporated to dryness, and the residue dried by heating slightly; to it 4 cc. HCl (1·12) and 20 cc. water were added; a large light yellow precipitate separated, showing that the thallic salt had been largely, but not completely, reduced.

P. 14, N. 1: *Explanation of the Solubility of* $PbSO_4$ *in Ammonium Acetate Solution.*—See Noyes and Whitcomb (*Journ. Am. Chem. Soc.*, 1905, xxvii., 747).

P. 14, N. 2: *Behaviour of Bismuth Compounds towards Ammonium Acetate and* K_2CrO_4.—Five mgrms. Bi as solid bismuth oxysulphate (see P. 26, N. 5) were treated by P. 14, 20 cc. normal ammonium acetate and 5 cc. 5 normal acetic acid being used; a yellow precipitate very similar in appearance to $PbCrO_4$ was formed on the addition of K_2CrO_4, but this dissolved quickly in the acetic acid. The experiment was repeated with 1 mgrm. Bi as nitrate; the result was the same.

P. 15, N. 1: *Molecular Formula of Gaseous Mercurous Chloride.*—Baker (*Journ. Chem. Soc. Trans.*, 1900, lxxvii., 646) has shown that absolutely dry mercurous chloride vapour has a density corresponding to the formula Hg_2Cl_2.

Condition of Mercurous Salts in Solution.—See Ogg (*Zeit. Phys. Chem.*, 1898, xxvii., 290—299; Abel (*Zeit. Anorg. Chem.*, 1901, xxvi., 377).

Action of NH_4OH *on* Hg_2Cl_2.—For the evidence that the black residue is a mixture of Hg and $HgClNH_2$, see Barfoed (*Journ. Prakt. Chem.*, 1889, xxxix., 201); Pesci (*Gazz. Chim. Ital.*, 1891, xxi., 569); and Sen (*Zeit. Anorg. Chem.*, 1903, xxxiii., 197).

P. 15, N. 3: *Complex Silver Ammonia Anions.*—See Bodländer and Fittig (*Zeit. Phys. Chem.*, 1902, xxxix., 597); Whitney and Melcher (*Journ. Am. Chem. Soc.*, 1903, xxv., 69); Bodländer and Eberlein (*Zeit. Anorg. Chem.*, 1904, xxxix., 197); Lucas (*Zeit. Anorg. Chem.*, 1904, xli., 193).

P. 15, N. 5: *Solubility of* AgCl *in Chloride Solutions.*—See Comey, ("Dictionary of Solubilities," p. 373).

One mgrm. Ag as AgCl was dissolved in 5 cc. NH_4OH (0·96), the solution obtained was made acid with HCl; no precipitate separated. The experiment was repeated, using HNO_3 instead of HCl; a precipitate formed. Five mgrms. Ag as AgCl were dissolved in 15 cc. NH_4OH (0·96), and the solution made acid with HCl; no precipitate separated. An equal volume of water was added; AgCl precipitated.

Precipitation and Separation of the Copper and Tin Groups.

P. 21, N. 1: *Order of Precipitation of the Sulphides of the Copper and Tin Groups from Cold* HCl *Solution.*—Two mgrms. As as As_2O_3, 2 mgrms. Hg, and 2 mgrms. Cu, each as chloride, were in separate experiments dissolved in 2 cc. HCl (1·20), and 2 mgrms. of each of the elements of the copper and tin groups were in separate experiments dissolved in 4 cc. HCl (1·12); each solution was put into a small bottle, saturated completely with H_2S at room temperature, the bottle corked, and allowed to stand fifteen minutes. In cases where no precipitate formed the solution was successively diluted with measured quantities of water, being again saturated with H_2S, and allowed to stand after each addition; the most strongly acid solution from which each element separated is shown by the following table:—

HCl (1·20).	HCl (1·12).	Water.	Elements precipitated.
Cc.	Cc.	Cc.	
2	..	0	As
..	4	0	Hg, Cu
..	4	4	Sb
..	4	12	Bi, Sn(ic)
..	4	44	Cd
..	4	96	Pb, Sn (ous)

The cadmium, lead, and stannous sulphides precipitated slightly, and only after several minutes; the others almost at once.

Order of Precipitation of the Sulphides of the Iron Group from Weak Acid Solutions.—Fifty mgrms. Zn and 500 mgrms. Zn as nitrate, 500 mgrms. Fe (ous), 500 mgrms. Ni, 500 mgrms. Co, and 500 mgrms. Mn as sulphate were

* From the *Technology Quarterly*, xix., No. 3, September, 1906.

in separate experiments dissolved in 1 cc. HCl (1·12), and 100 cc. water, saturated with H_2S at room temperature, and allowed to stand ten minutes; zinc was precipitated from both its solutions, but none of the other elements. The experiments with 50 mgrms. Zn and 500 mgrms. Zn were repeated, except that 2 cc. HCl (1·12) was used; ZnS precipitated after several minutes in the 500 mgrms. portion, but not in the 50 mgrms. one.

500 mgrms. each of ferrous Fe, Co, Ni, and Mn as sulphate were dissolved in 100 cc. water, and saturated at room temperature with H_2S for ten minutes; FeS slowly precipitated in considerable quantity, but none of the other sulphides.—The experiment was repeated, except that the substances were dissolved in 10 cc. 10 per cent acetic acid solution, 1 cc. 10 per cent $NaC_2H_3O_2$ solution, and 90 cc. water; the result was the same. The last experiment was repeated, except that 10 cc. instead of 1 cc. $NaC_2H_3O_2$ solution was used; large quantities of NiS and CoS as well as of FeS precipitated, but no MnS. In another experiment 500 mgrms. Mn as $MnSO_4$ were dissolved in 1 cc. 10 per cent $HC_2H_3O_2$ solution, 10 cc. 10 per cent $NaC_2H_3O_2$ solution, and 90 cc. water, and saturated with H_2S; no MnS precipitated.

P. 21, N. 3: *Precipitation of Arsenic, Platinum, and Molybdenum by* H_2S.—100 mgrms. As as H_3AsO_4, 100 mgrms. Mo as H_2MoO_4, and 25 mgrms. Pt as H_2PtCl_6 were dissolved in separate 100 cc. portions of dilute HCl, one volume HCl (1·12) to twenty-five volumes water, and were saturated with H_2S in the cold; less than 1 mgrm. of As and of Pt, but considerable Mo precipitated as sulphides in ten minutes. The three solutions were then filtered, heated to boiling, and saturated with H_2S, at that temperature for about fifteen minutes; a large precipitate resulted in each case. The solutions were filtered, saturated in the cold with H_2S, and heated in pressure bottles in the steam-bath for one hour; a considerable precipitate separated from each solution, estimated to contain about 5 mgrms. As in the arsenic solution, and 10 mgrms. Mo in the molybdenum solution.

100 mgrms. As as H_3AsO_4 were added to 100 cc. HCl (1·20), and saturated in the cold with H_2S; a large yellow precipitate separated. After five minutes the mixture was diluted with half its volume of water, and filtered; the filtrate was heated to 100°, and H_2S passed in for ten minutes; a small precipitate estimated to contain only 3 to 5 mgrms. As resulted. These two experiments with arsenic acid show that the precipitation takes place much more rapidly in the presence of concentrated HCl.

Precipitation of Cadmium and Lead by H_2S.—Separate solutions containing 5 mgrms. Cd, 5 mgrms. Pb, 10 mgrms. Cd, and 10 mgrms. Pb, respectively, in 100 cc. of a mixture of one volume HCl (1·12) and fifteen volumes water, were saturated in the cold with H_2S for fifteen minutes; precipitates began to form only after ten or fifteen minutes in each of the solutions.

Separate solutions containing 1 mgrm. Cd and 1 mgrm. Pb in 100 cc. of a mixture of one volume HCl (1·12), and twenty-five volumes water were saturated in the cold with H_2S; both solutions showed precipitates, but that in the case of lead was scarcely visible until it was collected on a filter. The PbS was filtered out, and NH_4OH and $(NH_4)_2S$ added to the filtrate; a brown colour corresponding to 0·1 to 0·2 mgrm. Pb resulted, showing that substantially all the lead was precipitated.

Precipitation of Zinc by H_2S.—Solutions containing 500 mgrms. Zn in three 100 cc. portions of dilute HCl, containing one volume HCl (1·12) to twenty-five volumes water, to forty volumes water, and to fifty volumes water, respectively, were saturated in the cold with H_2S, then heated to boiling, and again saturated with H_2S; in the cold, H_2S failed to produce a precipitate in any of the solutions in five minutes; but on heating, a slight precipitate formed in the 1 : 40, and a heavy one in the 1 : 50, but none in the 1 : 25 mixture.

Precipitation of Titanium Hydroxide by Hydrolysis.—Separate 100 mgrm. portions of Ti in 100 cc. dilute HCl, containing one volume HCl (1·12) to twenty volumes water, to ten volumes water, and to eight volumes water, respectively, were saturated cold with H_2S, and then heated in pressure bottles in a steam-bath for two hours; in the 1 : 20 volume solution a very large white precipitate had formed in thirty minntes; the 1 : 10 solution remained clear for forty-five minutes, and then showed only a turbidity; and the 1 : 8 solution remained unchanged during the two hours.

Precipitation of Bismuth and Antimony Oxychlorides by Water.—Separate solutions containing 500 mgrms. Bi as nitrate, 400 mgrms. Sb as $SbCl_3$, and 300 mgrms. Sb as Sb_2O_5 (obtained by evaporating an $SbCl_3$ solution with aqua regia) were evaporated with HCl almost to dryness; 4 cc. HCl (1·12) and 36 cc. water were added, and the mixture was heated; from the bismuth solution no precipitate separated either in the cold or upon heating; in the antimonous solution a large white precipitate formed in the cold, but dissolved almost completely upon heating, and in the antimonic solution a large precipitate separated in the cold, and did not appear to dissolve upon heating. To the bismuth solution 20 cc. more water were added; a white precipitate then began to form.

P. 21, N. 3; *Separation of the Copper and Tin Groups from the Iron Group by* H_2S.—Mixtures of elements as shown below were dissolved in 4 cc. HCl (1·12) and 36 cc. water, and treated exactly as described in P. 21, except that the solutions containing cadmium were diluted at once to 100 cc., and saturated at room temperature with H_2S; the solutions were filtered after ten to thirty minutes, the filtrate boiled to expel H_2S, HNO_3 added, the mixture again boiled, NH_4OH added to detect iron, any precipitate filtered off, and H_2S was passed into the filtrate, or $(NH_4)_2S$ was added to it to detect zinc, nickel, or cobalt; the results are recorded below as in the Test Analyses :—

Cd	500 —	500 —	500 —	500 —	500 —
Zn	0 S	2 S	1 S (*a*)	..	..
Fe	0 S	..	..	2 S	1 S
Ni	0 S	..	..	..	1 S
Cu	500 —	500 —	..	..	..
Bi	..	..	200 —	200 —	..
As (ous)..	..	..	100 —	100 —	..
Sb (ous)..	..	..	100 —	100 —	..
Sn (ic) ..	..	..	200 —	200 —	..
Zn	..	..	1 S (*a*)	..	..
Fe	1 S	0 S	..	..	..
Ni	1 S	..	..	1 S	..
Co	..	1 S (*b*)	..	..	..

(*a*) A nearly white precipitate was obtained with $(NH_4)_2S$.

(*b*) The black $(NH_4)_2S$ precipitate was dissolved in aqua regia, and the solution evaporated just to dryness; th residue had a slight pink colour.

P. 21, N. 4: *Composition of the* H_2S *Precipitates.*—From solution of $HgCl_2$ in excess, see Rose (*Pogg. Ann.*, 1828, xiii., 64). From arsenic acid solutions, see C. E., P. 44, N. 1, 2, and 3. From antimonic solutions, see Klenker (*Journ. Prakt. Chem.*, 1889, lix., 150). From chloroplatinic acid, see Antony and Lucchesi (*Gazz. Chim. Ital.*, 1896, xxvi., 211). From gold chloride, see Hoffmann and Krüss (*Ber.*, 1887, xx., 2369, 2704). From selenous acid, see Ditte (*Comptes Rendus*, 1871, lxxiii., 625, 660); Divers and Shimidzu (*Journ. Chem. Soc.*, 1885, xlvii., 441). From tellurous acid, see Becker (*Liebig's Ann. Chem.*, 1875, clxxx., 260).

P. 21, N. 5: *Action of* HNO_3 *on* H_2S.—Separate 50 cc. portions of mixtures of one volume of HNO_3 (1·20) in 2·5, 5, 10, and 20 volumes of solution were heated to boiling, and saturated with H_2S at that temperature; in the first solution a precipitate of sulphur soon appeared, in the second a slight precipitate formed after ten minutes, and in the last two no precipitates formed in twenty minutes.

P. 22, N. 1: *Solubility of* SnS *and* Sb_2S_3 *in Ammonium Monosulphide.*—See C. E., P. 22, N. 4.

P. 22, N. 2: *Hydrolysis of the Alkaline Sulphides and Composition of the Polysulphides.*—It has been shown by C. F. Sammet (Thesis, Massachusetts Institute of Technology, 1903) that a solution of the empirical composition $(NH_4)_2S$ containing 0·1 formula weight per litre is practically completely hydrolysed into NH_4OH and NH_4SH, and that in the same solution the latter is only slightly (roughly, 0·3 per cent) hydrolysed into H_2S and a second equivalent of NH_4OH. But in a solution containing only half as much NH_4OH, *i.e.*, in a solution containing 0·1 formula weight NH_4SH per litre, the degree of hydrolysis increases to several per cent.

Küster and Heberlein (*Zeit. Anorg. Chem.*, 1905, xliii., 71) have found Na_2S in a solution containing 0·05 formula weights per litre to be 86 per cent hydrolysed into NaOH and NaSH, and NaSH in 0·01 normal solution to be only 0·15 per cent hydrolysed into NaOH and H_2S. For the degree of hydrolysis of NaSH, Walker (*Zeit. Phys. Chem.*, 1900, xxxii., 137) found practically the same value by an independent method.

Küster and Heberlein also investigated the hydrolysis of the polysulphides of sodium, and showed that the degree of hydrolysis decreases with increasing sulphur content; thus a solution of the composition Na_2S_2 with 65 per cent, a solution of Na_2S_4, only 12 per cent hydrolysed. They found further that Na_2S solutions of the following concentrations when saturated with sulphur at 24° have the empirical composition Na_2S_x where x has the following values:—

Formula weights Na_2S per litre .	2·0	1	½	½
Value of x	4·48	4·84	5·12	5·24

It was found that x varied only slightly with the temperature. According to these authors, Na_2S_4, and less readily Na_2S_5, have been obtained in the solid form by evaporating aqueous solutions; but Na_2S_2 and Na_2S_3 have not been so obtained. All of these have, however, been crystallised from alcoholic solutions (H. Boettger, *Liebig's Ann. Chem.*, 1884, ccxxiii., 335; H. Rebs, *Liebig's Ann. Chem.*, 1888, ccxlvi., 358).

Bloxam (*Journ. Chem. Soc.*, 1894, lxvii., 300; 1900, lxxvii., 753) found that a very concentrated ammonium sulphide solution prepared from NH_4OH (0·88) so as to have exactly the composition $(NH_4)_2S$ dissolved sulphur until the composition became approximately $(NH_4)_2S_4{\cdot}5$. He has obtained under various special conditions the following solid salts:—$(NH_4)_2S_3$, $(NH_4)_2S_5$, $(NH_4)_2S_7$, $(NH_4)_2S_9$, $(NH_4)_4S_7$, and $(NH_4)_4S_9$; Na_2S, NaSH, Na_2S_5, and Na_4S_9; K_2S, KSH, K_2S_3, K_2S_4, K_2S_5, K_4S_5, and K_4S_9.

P. 22, N. 2: *Ammonium Salts of the Sulpho-acids.*—The following ammonium sulpho-salts have all been prepared in the crystalline form by adding alcohol to concentrated solutions of the sulphides in ammonium sulphide:—$(NH_4)_3AsS_3$ and $(NH_4)_3AsS_4$ (Berzelius, *Pogg. Ann.*, 1826, vii., 141 and 18); $(NH_4)_3SbS_3$ (Pouget, *Ann. Chim. Phys.*, 1899 [7], xviii., 532); $(NH_4)_3SbS_4$, $(NH_4)_3SbS_4{\cdot}4H_2O$ (Stanek, *Zeit. Anorg. Chem.*, 1898, xvii., 121); $(NH_4)_3SnS_3{\cdot}3H_2O$ and $(NH_4)_3SnS_3{\cdot}7H_2O$ (Stanek, *loc. cit.*, p. 213). Certain other arsenous salts, including NH_4AsS_2, have also been prepared in the solid state. On evaporating a solution of Sb_2S_3 in $(NH_4)_2S$ in a vacuum at a low temperature, the meta salt, NH_4SbS_2, is usually obtained; on evaporating at a high temperature, or on treating NH_4SbS_2 with water, solid $(NH_4)_2Sb_3S_7$ is formed. Berzelius states that a solution of the empirical composition $(NH_4)_2S$ saturated with As_2S_3 or As_2S_5 contains these substances in the proportion $As_2S_3 : 2(NH_4)_2S$ or $As_2S_5 : 2(NH_4)_2S$. Pouget finds that a solution of $(NH_4)_2S$ saturated with Sb_2S_3 contains less antimony than corresponds to the ratio $Sb_2S_3 : 3(NH_4)_2S$. A K_2S or Na_2S solution dissolves sufficient Sb_2S_3 to give a solution of the composition $Sb_2S_3 : 2K_2S$ or $Sb_2S_3 : 2Na_2S$. There does not appear to be any direct evidence as to the nature of these salts in solution.

*Solid sulpho-salts of the rare elements have been obtained from alkaline sulphide solutions as follows:—K_3AuS_3 (Antony and Lucchesi, *Gazz. Chim. Ital.*, 1896, xxvi., 359); $3K_2S.TeS_2$, $3Na_2S.TeS_2$, and $3(NH_4)_2S.TeS_2$ (Berzelius); K_2MoS_4, $(NH_4)_2MoS_4$ (Berzelius, *Pogg. Ann.*, 1826, vii., 429; Krüss, *Liebig's Ann. Chem.*, 1884, ccxxv., 29).

P. 22, N. 4: *Solubility of the Sulphides of the Tin and Copper Groups in Ammonium Hydroxides, Monosulphide, and Polysulphide.*—500 mgrms. As as As_2S_3, Sb as Sb_2S_3, Sn as SnS, Cu as CuS, Hg as HgS, Cd as CdS, Bi as Bi_2S_3, all freshly precipitated by H_2S, and 500 mgrms. As as As_2S_5, 100 or 500 mgrms. Sb as Sb_2S_5, and 100 or 500 mgrms. Sn as SnS_2 all precipitated from ammonium polysulphide, were warmed (but not enough to cause boiling through escape of gas) in a covered casserole for about five minutes with (i.) 15 to 20 cc. NH_4OH (0·96); (ii.) 10 cc. of the ammonium monosulphide reagent; and (iii.) 10 cc. of the ammonium polysulphide reagent. The solutions were then filtered and the filtrates acidified with HCl. The amount dissolved was estimated from the size and colour of the precipitate, or from the amount of the undissolved residue. The results are given below; the numbers represent roughly the number of mgrms. of the element dissolved, a + sign indicating that this amount dissolved readily, and that probably much more would have dissolved.

	(i.) NH_4OH (0·96).	(ii.) Monosulphide.	(iii.) Polysulphide.
As_2S_3 ..	500 +	500 +	500 +
As_2S_5 ..	500 +	500 +	500 +
Sb_2S_3 ..	0·5—1	50—100	500
Sb_2S_5 ..	100 (*a*)	300	500 +
SnS ..	0 (*b*)	0—3 (*b*)	500
SnS_2 ..	100 (*a*)	300	500 +
CuS ..	0—0·3	0	5—10
HgS ..	3—10	0	1
CdS ..	0	0	0
Bi_2S_3 ..	0	0	0

(*a*) Only about 100 grms. of the element as sulphide was taken in these experiments.

(*b*) A few mgrms. (5 to 15) of a yellow precipitate (SnS_2), containing little or no SnS were precipitated on acidifying the filtrate.

The orange Sb_2S_3 was found to be changed into the black variety, stibnite, by continued treatment with ammonium monosulphide, and black HgS was changed into the red modification by continued treatment with the polysulphide. It was also noted that the HgS which dissolves in NH_4OH may be precipitated by adding a few drops of monosulphide.

500 mgrms. Cu and 500 mgrms. Hg as freshly precipitated sulphides were in separate experiments warmed to 50° or 60° in covered casseroles with 25 cc. ammonium monosulphide for fifteen minutes; the residues were filtered off, and the filtrates made acid with HCl; a slight precipitate of sulphur separated, which was only very slightly darkened, thus showing that only an insignificant quantity of CuS or HgS had dissolved.

An ammonium monosulphide solution was prepared from NH_4OH (0·90) as described in N. 2, except that the solution was not diluted with the equal volume of water. From this solution several different ammonium polysulphide solutions were prepared, containing, respectively, 20, 10, 5, 3, and 1 grms. dissolved sulphur in 200 cc., and their solvent power for SnS and CuS tested as follows:—

500 mgrms. Sn as freshly precipitated SnS were warmed gently in a covered casserole with (i.) 10 cc. of these undiluted solutions; (ii.) 5 cc. of them + 5 cc. water; and (iii.) 5 cc. of them + 10 cc. water. The mixture was stirred frequently with a glass rod. The amount of tin in mgrms. dissolved in a solution containing x grms. dissolved sulphur in 200 cc., and the time required to dissolve it are given below.

	x=10 grms.	x=5 grms.	x=3 grms.	x=1 grm.
(i.) 10 cc. undiluted	500 / 4 mins.	500 / 5 mins.	500 / 15 mins.	100 / 5 mins.
(ii.) 5 cc. + 5 cc. H_2O ..	500 (*a*) / 5 mins.	500 / 10 mins.	.. / ..	100 / 10 mins.
(iii.) 5 cc. + 10 cc. H_2O	500 / 8—10 mins.	..	..	..

500 mgrms. Cu as CuS were similarly treated for five minutes; the following table shows roughly the number of mgrms. Cu as CuS that dissolved in a solution containing x grms. dissolved sulphur in 200 cc. where x has the stated values.

x = grms.... ... 20	10	5	3	1	0
(i.) 10 cc. of solution .. 25 +	..	12	6	0·5	..
(ii.) 5 cc. + 5 cc. H_2O ..	8 (*a*)	4	3	0·2	0
(iii.) 5 cc. + 15 cc. H_2O ..	6—8	..	..	..	..

(*a*) The regular reagent described in N. 2 has this composition.

P. 22, *N. 5: *Solubility of the Sulphides of the Rarer Elements in Ammonium Sulphide.*—Ribau (*Bull. Soc. Chim.*, 1877, xxviii., 241) has shown that pure, freshly precipitated PtS_2 is nearly insoluble in ammonium sulphide, but dissolves in large quantity when mixed with sulphides of either the tin or copper groups. (Under "Test Analyses of the Tin Group" it is shown that small quantities of platinum and gold divide almost equally between the copper and tin groups when copper is also present).

50 mgrms. Mo as freshly precipitated sulphide were digested in a covered casserole at 40—60° with 25 cc. ammonium monosulphide for fifteen minutes; the deep red solution was filtered and acidified with HCl; a precipitate estimated to contain about 35 mgrms. Mo separated. The residue was digested a second time with 25 cc. ammonium monosulphide; only about half the residue dissolved. (The experiment was repeated, using 10 cc. portions of ammonium polysulphide; the result was the same, about two-thirds dissolving in the first treatment and about half the residue in the second).

200 mgrms. Te were freshly precipitated with H_2S from a hot HCl solution containing 4 cc. HCl (1·12) and 36 cc. water; the black precipitate was digested with 25 cc. ammonium monosulphide; the precipitate dissolved completely in three or four minutes. The solution was acidified with HCl; a black precipitate separated. This was digested with 10 cc. ammonium polysulphide; it dissolved immediately. To the solution HCl was added; a black precipitate separated.

200 mgrms. Se as H_2SeO_3 were precipitated by Na_2SO_3 in an HCl (1·12) solution, as in *P. 43*c*. The red precipitate was filtered off and washed with HCl (1·12). It was then dissolved in hot HNO_3 (1·20); the solution was evaporated just to dryness and the residue dissolved in 4 cc. of HCl (1·12) and 36 cc. of water. The solution was heated to boiling and saturated with H_2S. A yellow precipitate which partly changed to red during the precipitation was produced. The solution was diluted to 100 cc. and again saturated with H_2S in the cold; the precipitate was filtered off and digested with 25 cc. ammonium monosulphide; the finely divided portion of the precipitate dissolved in a few minutes, forming a deep red solution, but the larger particles turned black on the surface and dissolved very slowly. After a few minutes the solution was filtered and the black residue digested successively three times with a fresh 25 cc. portion of ammonium monosulphide; finally it all dissolved. The successive sulphide solutions were acidified with HCl (1·12); a bright yellow precipitate formed at first in every case, but that in the first solution gradually became orange within a few hours.

P. 22, N. 6: *Extraction by Ammonium Monosulphide and Polysulphide of Arsenic, Antimony, and Tin Sulphides from those of the Copper Group.*—See "Test Analyses of Tin Group."

Mixtures of 5, 10, 15, and 20 mgrms. Sn as SnS with 500 mgrms. Cd as CdS were digested at 80—90° with the ammonium polysulphide reagent in a pressure bottle for half an hour, and the solutions were analysed by P. 41—47; the results recorded as in the Test Analyses were as follows:—

Cd	500	500	500	500
Sn	5 F	10 F	15 D	20 S

The confirmatory test for tin (P. 47) failed in the experiment with 15 mgrms. Sn. — The experiment was repeated with a mixture of 5 mgrms. Sn as SnS_2 and 500 mgrms. Cd as CdS; a small but satisfactory test for tin was obtained.

P. 22, N. 8: *Coagulation of Colloidal Sulphides by* NH_4NO_3.—In washing the various sulphides of the copper groups after the $(NH_4)_2S$ treatment, CuS, and especially CdS, sometimes passed through the filter in colloidal condition. To these colloidal mixtures was added enough solid NH_4NO_3 to make a 5 per cent solution, and the mixtures were shaken and filtered; the filtrates were clear.

(To be continued).

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

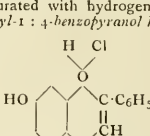
Ordinary Meeting, May 16th, 1907.

Prof. R. MELDOLA, F.R.S., Past President, in the Chair.

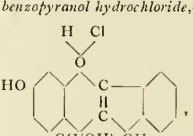
(Concluded from p. 274).

108. "*Some Derivatives of γ-Pyranol allied to certain Derivatives of Brazilein and Hæmatein.*" (Preliminary Communication). By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

o-Hydroxybenzaldehyde and its derivatives condense with certain acetophenone or hydrindone derivatives to form derivatives of γ-pyranol. Thus β-resorcylaldehyde and acetophenone condense readily when their solution in acetic acid is saturated with hydrogen chloride, and the *7-hydroxy-2-phenyl-1 : 4-benzopyranol hydrochloride*,—

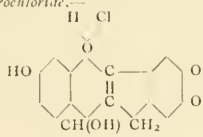


thus produced, is identical with the substance prepared by Bulow and Sicherer (*Ber.*, 1901, xxxiv., 3890) from benzoylacetaldehyde by condensation with resorcinol. If the acetophenone is replaced by 1-hydrindone, *7-hydroxy-2 : 3-indeno-1 : 4-benzopyranol hydrochloride*,—



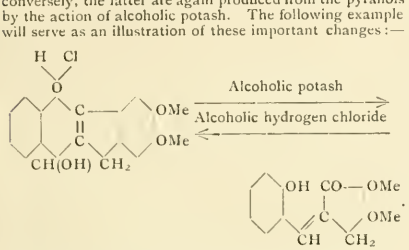
is produced. This substance crystallises with 2 molecules of water and yields, with platinum chloride, the double *salt* $(C_{16}H_{12}O_3,HCl)_2PtCl_4$ and, with gold chloride, the *salt* $C_{16}H_{12}O_3HCl,AuCl_3,H_2O$.

7-Hydroxy-5 : 6-dimethoxy-2 : 3-indeno-1 : 4 benzopyranol hydrochloride.—



is obtained when 3-resorcylaldehyde and 5 : 6-dimethoxy-1-hydrindone are condensed by hydrogen chloride in methyl-alcoholic solution. Similar condensations have also been carried out with salicylaldehyde and *p*-methoxysalicylaldehyde and 5 : 6-dimethoxyhydrindone.

The pyranol derivatives thus produced may also be obtained by the action of alcoholic hydrochloric acid on the corresponding *o*-hydroxybenzylidene-1-hydrindones, and, conversely, the latter are again produced from the pyranols by the action of alcoholic potash. The following example will serve as an illustration of these important changes :—



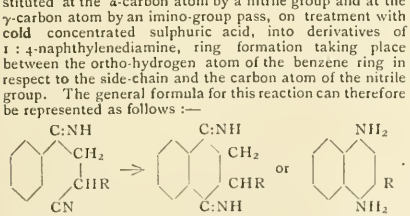
The authors wish to reserve, for a short time, the further investigation of the above and similar condensations.

109. "*Arsenic Di-iodide.*" By JOHN THEODORE HEWITT and THOMAS FIELD WINMILL.

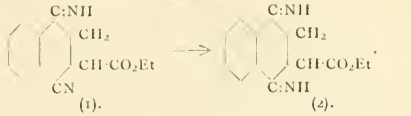
The authors have prepared and analysed the arsenic di-odide described by Bamburger and Philipp (*Ber.*, 1881, xiv., 2643). The molecular weight determined by the elevation of boiling point in carbon disulphide solution shows the compound to have the formula As_2I_4. The substance is, however, useless for the preparation of aromatic analogues of cacodyl, since the only product isolated from the action of magnesium phenyl bromide is triphenylarsine. Pyridine decomposes the compound immediately with liberation of arsenic.

110. "*The Formation and Reactions of Imino-compounds.* Part IV. *The Formation of 1 : 4-Naphthylenediamine from Ethyl γ-imino-α-cyano-γ-phenylbutyrate.*" By JOCELYN FIELD THORPE.

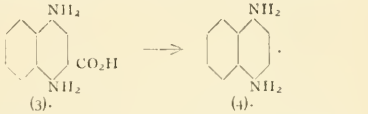
In continuation of the work already published in Parts II. and III. of this series it was shown that derivatives of benzene having a side-chain of three carbon atoms substituted at the α-carbon atom by a nitrile group and at the γ-carbon atom by an imino-group pass, on treatment with cold concentrated sulphuric acid, into derivatives of 1 : 4-naphthylenediamine, ring formation taking place between the ortho-hydrogen atom of the benzene ring in respect to the side-chain and the carbon atom of the nitrile group. The general formula for this reaction can therefore be represented as follows :—



Ethyl γ-imino-α-cyano-γ-phenylbutyrate (1) passes on treatment with cold concentrated sulphuric acid into ethyl 1 : 4-naphthylenediamine-3-carboxylate (2) :—



This ethyl salt yields 1 : 4-naphthylenediamine-3-carboxylic acid (3) on hydrolysis, from which 1 : 4-naphthylenediamine (4) can be prepared on heating at 200° in a current of hydrogen :—



111. "*Mercury Derivatives of Pseudo-acids containing the Group* ·CO·NH·." By SAMUEL JAMES MANSON AULD.

Unlike cyanuric acid, which forms two isomeric mercuric salts (Hantzsch, *Ber.*, 1902, xxxv., 2717), all the pseudo-acids containing the group ·CO·NH· examined have given only one derivative, in all cases an N-salt containing the group ·CO·NHg·. Some of these N-mercury salts act as "mercury acids" and form alkali salts. Violuric acid, for instance, forms a series of coloured alkali mercuriviolurates, which can be obtained both in the hydrated and anhydrous states. The pseudo-acids examined include uric acid and its alkyl derivatives, ψ-uric acid, methyluracyl, violuric and dimethylviolurie acids, saccharin, benzoylcyanamide, and carbostyril.

112. "*The Influence of Substitution in the Nucleus on the Rate of Oxidation of the Side-chains.* III. *Oxidation of the Nitro- and Chloronitro-derivatives of Toluene.*" By JULIUS BEREND COHEN and HENRY JAMES HODSMAN.

The authors have studied the rate of oxidation of the nitro- and chloronitro-toluenes, the same method being employed as that previously described (*Trans.*, 1904, lxxxv., 174, 1622). Excluding the 4-chloro-2-nitrotoluene, which occupies an exceptional position in the series, the general result of the oxidation of the ten isomeric chloronitrotoluenes may be summarised as follows. The compounds with the nitro-group in the ortho-position are least oxidised, those with the nitro-group in the para-position are most oxidised, whilst the meta-compounds stand midway between the two. The same result is obtained with the three isomeric nitrotoluenes. The position occupied by 4-chloro-2-nitrotoluene appears to depend on the length of time during which the substance is in contact with the oxidising agent, the quantity of acid formed varying inversely with the time of oxidation. This has been explained by showing that in all the *o*-nitro-compounds the acid first formed undergoes further oxidation, and that this is especially the case with the 4-chloro-2-nitro-compound. The result is that the quantity of acid as well as the total yield of products is low ; in other words, the more protracted the oxidation, the more of the acid, first formed, is destroyed.

The authors also described the preparation of 3-chloro-2-nitrotoluene which was originally obtained by one of them in conjunction with H. G. Bennett, so that all the isomeric chloronitrotoluenes are now known.

113. "*The Reducibility of Magnesia by Carbon.*" (Preliminary Note). By ROLAND EDGAR SLADE.

Three distinct methods were attempted for establishing the reducibility of magnesia by carbon. The first consists in heating magnesia and carbon together in an enclosed furnace, with arc or resistance heating, and collecting and analysing the gaseous products of reaction ; considerable quantities of carbon monoxide and some carburised magnesium were in this way obtained.

The second method is an application of that employed by R. S. Hutton and J. E. Petavel (*Proc. Roy. Soc.*, 1907,

A, lxxix., 155) for investigating the reduction of alumina, and consists in employing a bath of molten electrolytic copper as a solvent and condenser for the metal vapour.

These experiments were carried out in carbon tube furnaces and in crucibles heated under the electric arc; alloys of copper and magnesium were obtaind at temperatures as low as 1700°. In the carbon tubes the sublimed magnesia also reacts with the heated walls of the tubes, from which a powder containing carburised magnesium can be collected on cooling.

The third method has not up to the present proved successful, but consists in heating a mixture of magnesia and carbon to known temperatures in a current of nitrogen gas, the product being examined for nitride. The temperature of reduction of magnesia seems to be above the limit of temperature at which the nitride is stable.

The two methods which have furnished a positive result give independent confirmation of the recent experiments of Lebeau (*Comptes Rendus*, 1907, cxliv., 799). Whereas this author considers that the reduction only occurs at or above the boiling point of magnesia when the vapour of carbon and magnesia come in contact, the present research seems to show that the reaction can take place at temperatures below the melting-point of this oxide.

114. "*The Reaction between Organo-magnesium Halides and Nitro-compounds.*" (Preliminary Note). By ROBERT HOWSON PICKARD and JOSEPH KENYON.

Aromatic nitro-compounds react very vigorously with an organo-magnesium halide in ethereal solution.

p-Nitrotoluene thus forms an indefinite amorphous yellow *compound*, which, when treated with acids, yields principally *p*-nitrosotoluene, *p*-tolylhydroxylamine, *pp'*-azoxytoluene (probably by the interaction of the two former compounds), and *p*-toluidine.

The authors wish to reserve for a time the study of this new reaction.

115. "*A Method for the Determination of the Equilibrium in Aqueous Solutions of Amines, Pseudo-acids and Bases, and Lactones.*" By TOM SIDNEY MOORE.

The compounds mentioned in the title resemble each other in that their aqueous solutions contain, in addition to ions, two non-ionised forms. The relations may be represented by the equations :—

For a pseudo-acid— $$H\cdot X:O \underset{}{\overset{(1)}{\rightleftharpoons}} X\cdot OH \overset{(2)}{\rightleftharpoons} XO' + H\cdot.$$

For an amine— $$NX_3 + H_2O \overset{(1)}{\rightleftharpoons} NX_3H\cdot OH \overset{(2)}{\rightleftharpoons} NX_3H\cdot + OH'.$$

The reaction constants of the reactions (1) and (2) cannot in general be determined directly, although their determination is a matter of considerable importance; for the constant of reaction (2) is the true ionisation constant of the acid or base; and the constant of reaction (1) represents the relation between the two forms of the pseudo-acid, or between the amine and its hydroxide as the case may be.

The author showed that these constants, as well as their temperature coefficients, may be calculated from the results of measurements of the partition of the substance between water and another solvent, and of the "apparent" ionisation constant (as calculated from the electrical conductivity, or from degree of hydrolysis of salts) at different temperatures.

116. "*The 'True' Ionisation Constants, and the Hydration Constants of Piperidine, Ammonia, and Triethylamine.*" By TOM SIDNEY MOORE.

The equations developed in the preceding paper were applied to the results of the partition experiments of Hantzsch and Sebaldt, Hantzsch and Vagt, and of Dawson and McCrae, and the values of the true ionisation constants (k_1) and of the hydration constants (k_2) determined for different temperatures.

$k_2 C_{NX_3} = C_{NX_3HOH}$ and $k_1 C_{NX_3HOH} = C_{NX_3H^+} \times C_{OH^-}$.

At 20° the results were :—

	$k_1 \times 100$.	k_2.
Piperidine	0·156	2·83
Ammonia	0·0052	0·56
Triethylamine	0·064	1·86

Further, the heat of neutralisation of the three bases and the heat of solution of ammonia were calculated and found to agree satisfactorily with the experimental values.

PHYSICAL SOCIETY.

Ordinary Meeting, May 24th, 1907.

Prof. J. PERRY, F.R.S., President, in the Chair.

A PAPER on "*The Measurement of Mutual Inductance by the aid of a Vibration Galvanometer*," was read by Mr. A. CAMPBELL.

The measurement of mutual inductance is of importance not only in electrical science but also in electrotechnics; for example, it forms the basis of the magnetic testing of iron by the ballistic method. Carey Foster's method of comparing a mutual inductance with a capacity is one of the most convenient methods, and the formula is very simple, being $M = KR\gamma$, where K is the capacity (in farads) and R and r are resistances. The great advantage gained by the use of a *vibration galvanometer* in methods for measuring capacity or inductance (*e.g.* Wien's methods and Anderson's as used by Rosa and Grover) led the author to apply it to the Carey Foster and the Hughes-Rayleigh methods. He found, however, that with alternating currents it was necessary to modify the Carey Foster method by adding a series resistance in the condenser branch; this left the formula $M = KR\gamma$ unaltered and gave an additional formula involving the ratio of a mutual and a self inductance. It turned out that this modification had been suggested by Rowland. The modified method is extremely convenient, the two adjustments required for a balance being independent and the result not involving a knowledge of the frequency; the use of the vibration galvanometer is a great improvement, making the method independent of the wave-form of the current used. The author next discussed vibration galvanometers. They belong to the class of tuned (or resonance) instruments, the use of which in such measurements is due to Max Wien, whose work on the subject, beginning with his tuned optical telephone in 1891, is of the utmost value, and includes many methods which are now standard. If the detecting instrument used in a null method (with alternating current) is adjusted so that its natural period is in tune with that of the applied voltage, it will be set into strong resonance and will be enormously increased in sensitivity for this particular frequency, practically ignoring in comparison all the other components of the wave-form. Thus in any method in which the tuned instrument is used, a sine wave-form may be assumed. Rubens brought out his vibration galvanometer in 1896, the moving part being small soft-iron needles (on a torsion wire) polarised by a pair of magnets with polar windings carrying the current to be measured.

The author exhibited a vibration galvanometer of another type, having a moving coil controlled by an adjustable bifilar suspension. By adjusting the tension of this the tuning is very easily effected. For measuring the frequency to which a tuned instrument is responding, it is convenient to use the Hughes-Rayleigh method, in which a known self-inductance is compared with an unknown mutual inductance, the balance being dependent on the frequency. The author showed such an arrangement in which the slide-wire was graduated directly in frequency ($\sim$ per sec.). With accurately known frequency, on the other hand, the method gives absolute values of L and M.

In conclusion the author gave results of tests (by several methods) of a standard mutual inductance of 0·05 henry. The Kirchhoff method with direct deflection on a ballistic

galvanometer (of measured time of swing) gave a mean of 0·05014 henry, while the Carey Foster method gave 0·05009 henry; the probable error of the latter was much smaller than that of the older method.

Mr. A. Russell thanked the author for his most interesting and instructive demonstration. He considered that the bifilar method of suspending the vibrating coil was a great improvement on the single wire method described by Wien in the *Annalen der Physik* in 1901. In the *Physical Review* of last December Mr. Wells states that an alteration of 0·3 per cent in the length (about 12 cm.) of the stretched wire of a vibration galvanometer, when tuned, diminished the amplitude of the oscillation to less than one-fifteenth of its former value. The resonance point is very sharply defined. Hence to work such an instrument at its greatest sensibility, it must be most accurately tuned and it must be supplied with a current of almost absolutely constant frequency. When used to measure currents, the shape of the wave must be known. Mr. Campbell, however, apparently uses his vibration galvanometer mainly in null methods, and so any kind of interrupted or alternating current can be used, the shape of the wave being almost immaterial. He noticed that Mr. Campbell obtained his balance very rapidly by adjusting both the tension of the suspending spring of his galvanometer and, by means of a simple interrupting device, the frequency of the supplied current during the course of the same experiment. The suggested method of measuring frequency was extremely ingenious. He asked whether Mr. Campbell had found it necessary to take into account the "effective internal resistance" of the condensers he used in his tests.

Dr. Eccles asked the author for information as to the differences in performance between vibration galvanometers like the one shown, which employed rotational vibrations, and string galvanometers such as that of Einthoven, where the vibrations are transverse. The latter is a tuned instrument, and, it has been stated, has been used in the measurement of inductance, with what method and degree of success Mr. Campbell might know.

Mr. Rollo Appleyard said the author's methods should be applicable to the case of an inductance shunted by a capacity. In that event it would be useful for measurements of the inductance of telephone cables. If it could be adapted to that purpose, it would be of great service in affording a rapid means of determining the "attenuation constant," when frequency was of importance.

Dr. R. S. Willows said the suspension used by the author was an improvement on those in general use, which were liable to be broken when changing the frequency.

Mr. Campbell, in reply to Mr. Russell, said that the second formula in the modified Carey Foster method involved the resistance in series with the condenser. With a mica condenser it gave results in such close agreement with the first formula, that it precluded the possibility of any apparent resistance in the condenser of the order observed in certain condensers by Rowland and by Mr. Russell. The author was not aware of the use of the Einthoven string galvanometer as a vibration galvanometer, but if the damping could be made small enough there seemed no reason why it should not be so used. In reply to Mr. Appleyard, he thought that one of M. Wein's methods would be applicable.

A "*Note on the Rate of Decay of the Active Deposit from Radium*," by Messrs. W. Wilson and W. Makower, was taken as read.

In some experiments in which the ionisation produced by the α-rays from radium C was balanced against that produced by the more penetrating β- and γ-rays, it was found that after a short time these two ionisations were no longer exactly equal, however carefully they had been adjusted to equality at first. A similar effect had been noticed by Brousson, and was attributed to the slowly-moving β-rays emitted by radium B which is present with the radium C. Since these rays are emitted by radium B, whereas the α and more penetrating β-rays are emitted by radium C, it is to be expected that the rate of decay as measured by these two types of radiation will be different. The authors' experiments test this point, and confirm the view that the observed difference in the rate of decay as measured in the two vessels is due to the slowly-moving β-rays emitted by radium B.

Mr. S. G. Brown exhibited Apparatus for Relay Working of long Submarine Telegraph Cables. (In the absence of Mr. Brown the apparatus was described by Mr. A. E. Powell.)

In dealing with the question of the design of a relay for long cable work conditions and difficulties differing from long-distance telegraphy on land-lines are met with. Firstly, the minute currents recorded at the end of a long cable, when worked at its limit of speed, necessitate an instrument of high sensitiveness. Secondly, there is the difficulty of making and breaking contact with the usual form of "Butt" contact owing to insufficient pressure to break through surface oxidation, or if contact be satisfactorily made, the want of power to break away again due to coherence of the contact surfaces. Thirdly, the variation from the neutral position of a relay-tongue fixed to the coil of a receiving instrument due to the unequal charging up of the cable and receiving condensers necessitates some method of straightening out the zero. Mr. Brown's relay system therefore consists of three parts:—(1) The actual relaying device or "drum relay"; (2) an inductive shunt with closed iron circuit for use across the receiving coil to curb the signals and straighten out the zero; and (3) a method of applying a local current possessing suitable time-lag to the receiving coil to correct the tendency of signals made up of two or more impulses of the same polarity to fall away to zero due to the charging-up of the receiving condenser itself. The action of the drum relay and the details of the apparatus were described, and the running intruments were exhibited after the meeting.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 20, May 21, 1907.

Direct Hydrogenation of Diketones.—Paul Sabatier and A. Mailhe.—When diacetyl, $CH_3.CO.CO.CH_3$, an α-dione, is subjected to hydrogenation in presence of reduced nickel at 140—150°, it is totally transformed into nearly equal volumes of 2—3-butanolone and 2—3-butanediol. When a β-dione, such as acetylacetone, is similarly treated, three-quarters of it undergoes the reaction $CH_3.CO.CH_2.CO.CH_3 + H_2 = CH_3.COH + CH_3.CO.CH_3$, the alcohol and aldehyde being then further hydrogenated to form ethyl and isopropyl alcohol. One-quarter of the acetylacetone is hydrogenated normally, $CH_3.CO.CH_2.CO.CH_3 + H_2 = CH_3.CHOH.CH_2.CO.CH_3$. This second reaction tends to become less important as the temperature is raised, so that even at 180° it is diminished. The γ-dione, 2—5-hexanedione, yields the stable anhydride of diallyldihydrate, $CH_3.CHOH.CH_2.CH_2.CHOH.CH_3$, which is probably itself first formed and then dehydrated.

Explosive Mixtures of Air and Ether.—J. Meunier.—The superior limit of the inflammability of ether appears to be approximately 200 mgrms. per litre of air. At the lower limit, 58 or 60 mgrms. to the litre, it burns slowly without any explosion. When 1 or 2 mgrms. only are present the ether will not burn; from 100 to 175 mgrms. the explosion is violent, being at its maximum between 120 and 150 mgrms. From 175 to 200 mgrms. the violence of

the explosion decreases, and above 200 mgrms. the ether acts as an extinguisher upon a lighted match.

Catalytic Dehydration of Alcohols by Amorphous Phosphorus and Phosphates.— J. B. Senderens.—When amorphous phosphorus acts on ethyl alcohol it decomposes it into water and ethylene, the action increasing with the temperature, and a convenient method of preparing olefines can be based upon this fact. As, however, the catalytic power of phosphorus varies with different specimens, it is better to use the phosphates, aluminium phosphate being specially active. The alcohols of the cyclic series can also be dehydrated by this method, which can be applied to other organic compounds. Moreover, the silicates or silica can be substituted for the phosphates, and silica acts as a dehydrogenating or dehydrating catalyser, according as it is used in the crystalline or amorphous state.

Action of Magnesium Amalgam on Aldehydes.— André Kling and Paul Roy.—When magnesium amalgam acts on ethyl aldehyde a violent reaction occurs, and it is necessary to dilute the aldehyde with benzene and cool the vessel in which the operation is carried out. The author used benzene as a solvent, and poured the product of the reaction into cold water containing a little sulphuric acid, separated off the benzene layer and distilled it. The aqueous solution was neutralised with potassium carbonate, evaporated to dryness at 40°, taken up with chloroform, and re-distilled. It was then found that the product of the reaction is the glycol of aldol. With propyl alcohol the reaction is less energetic, the product being 2-methyl-1 . 3-pentanediol. Apparently the aldehyde and magnesium first form the compound $CH_3-C\overset{O-Mg}{\underset{H}{<}}CH_2>C\overset{H}{<}OH$, which decomposes with water, thus:—

$$CH_3-C\overset{O-Mg}{\underset{H}{<}}CH_2>C\overset{H}{<}OH + 2H_2O =$$
$$= CH_3C\overset{OH}{\underset{H}{<}}CH_2-C\overset{H}{<}OH + Mg(OH)_2.$$

Double Compounds of Aluminium Sesquisulphide with Monosulphides of Chromium, Nickel, Cobalt, and Magnesium.—Marcel Houdard.—When a mixture of aluminium and chromium is heated in sulphuretted hydrogen a blackish red crystalline residue is obtained, the analysis of which shows that it consists of $Al_2S_3.CrS$. When nickel and aluminium (in the proportion $Al_2 : Ni$) are fused together in sulphuretted hydrogen, a well crystallised black mass is obtained, which gives with water red crystals turning black. No definite compound could be isolated. Cobalt behaves similarly. With magnesium and aluminium a compound is obtained, $Al_2S_3.MgS$, corresponding to spinelle, $Al_2O_5.MgO$.

Dissociation of Lithium Silicates.—Edgard Derome.—When lithium silicate is dissociated in an exhausted porcelain tube in an electric furnace it is found that the rate of dissociation decreases very slowly at first, diminishing rapidly when the limit $SiO_2.2Li_2O$ is reached. In another series of experiments the pure crystalline $SiO_2.Li_2O$ was prepared by heating to a red heat for six hours in an open crucible a mixture of 5 SiO_2 and 2 Li_2O in suspension in fused lithium chloride. The rate of dissociation of this silicate continually decreases, the decrease becoming very rapid as $5SiO_2.Li_2O$ is approached, and apparently this last silicate is very little dissociated at 1300°; the micro-chemical examination of the residue showed that it consisted of lamellæ of $5SiO_2.Li_2O$. Probably this silicate also would dissociate if it were heated long enough.

Paraoxybenzoate of Calcium.—Œchsner de Coninck.—At 15° with a small quantity of water calcium paraoxybenzoate forms a crystalline monohydrate. When excess of water at 18° is added the salt begins to dissolve, and solution may be hastened by stirring with a glass rod, the last particles which dissolve showing the phenomenon of triboluminescence. Clear aqueous dilute solutions of calcium paraoxybenzoate deposit on standing a light downy mass, like a flocculent precipitate. This is totally insoluble, and consists of a mixture of several hydrates, the trihydrate predominating among them. The specific gravity of an aqueous solution increases with the concentration. Anhydrous calcium paraoxybenzoate combines with pure methyl alcohol, but not with ethyl alcohol.

Products of Condensation of Ethyl Oxalate with Dimethylaniline in presence of Aluminium Chloride.—A. Guyot.—The first product of the reaction between ethyl oxalate and dimethylaniline in presence of aluminium chloride is ethyl *p*-dimethylamidophenylglyoxalate, $(CH_3)_2N-C_6H_4-CO-CO_2C_2H_5$, the yield being about 60 per cent of the theory. The secondary product is ethyl tetramethyldiamidodiphenylglycolate,—

$$[(CH_3)_2N-C_6H_4]_2COH.CO_2C_2H_5.$$

This substance dissolves in acetic acid, giving an indigo-blue coloration, and condenses with tertiary aromatic amines in aqueous solution, either neutral or acid, giving derivatives of triphenylmethane, according to the equation

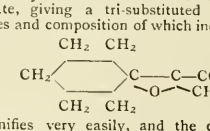
$$(CH_3)_2N-C_6H_4>C<\begin{matrix}OH\\CO_2C_2H_5\end{matrix} + R_2N-C_6H_5 =$$
$$= (CH_3)_2N-C_6H_4>C<\begin{matrix}(CH_3)_2N-C_6H_4\\R_2N-C_6H_4\end{matrix}-CO_2C_2H_5.$$

In concentrated sulphuric acid it forms a yellow solution, which, when heated to 140°, gives up carbon monoxide, and yields tetramethyldiamidobenzophenone,—

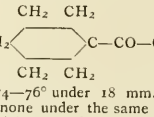
$$(CH_3)_2N-C_6H_4>C<\begin{matrix}OH\\COOH\end{matrix} =$$
$$= CO + H_2O + \begin{matrix}(CH_3)_2N-C_6H_4\\(CH_3)_2N-C_6H_4\end{matrix}>CO.$$

The ultimate product of the condensation of ethyl oxalate with dimethylaniline is ethyl hexamethyltriamidotriphenyl acetate, $[(CH_3)_2N.C_6H_4]_3C-CO_2C_2H_5$. This compound is also formed—(1) when ethyl dimethylamidophenylglyoxalate condenses with dimethylaniline in presence of phosphorus oxychloride or aluminium chloride; (2) when ethyl tetramethyldiamidodiphenylglycolate condenses with dimethylaniline at 100° in hydrochloric or acetic acid; (3) when ethyl tetramethyldiamidodiphenylamido acetate condenses with dimethylaniline at 100° in hydrochloric or acetic acid; (4) when ethylglyoxyl condenses with dimethylaniline at 100° in absence of any chlorinating agent, the principal product of the reaction being ethyldimethylamidophenylglyoxalate.

Synthesis of Hexahydroaromatic Ketones.—G. Darzens.—Cyclohexanone condenses with ethyl α-chloropropionate, giving a tri-substituted glycide ether, the properties and composition of which indicate that it is—



It saponifies very easily, and the corresponding acid decomposes when distilled *in vacuo*, giving hexahydroacetophenone,—



which boils at 74—76° under 18 mm. pressure. Orthomethylcyclohexanone under the same conditions yields a glycide ether, which, when distilled *in vacuo*, decomposes into carbon dioxide and orthomethylhexahydroacetophenone, which boils at 77—80° under 18 mm. pressure. Paramethylcyclohexanone and the meta-compound also yield glycide ethers, but more complicated ketones, such as

menthone and pulegone, do not form the corresponding compounds.

Metallic Thiocarbamates. Preparation of Thiocarbamides of the Fatty Series.—Marcel Delépine.—When soda and carbon disulphide act upon an amine in aqueous solution and dibasic lead acetate is added, the following reactions occur :—

$$RNH_2 + CS_2 + NaOH = RNH.CS_2.Na + H_2O,$$

$$RNH.CS_2.Na + HO.Pb.CO_2CH_3 = RN:CS + H_2O + PbS + CH_3.CO_2.Na.$$

The solutions when evaporated give crystalline salts which suffer double decomposition with metallic salts. Many of these salts decompose with water, giving thiocarbamide. With secondary amines, sodium salts of the constitution R_2 or RR'N.CS.SNa can be prepared by the same method. These latter also undergo double decomposition with metallic salts. Experiments with dimethyl piperidyl and diisobutyl thiocarbamates of sodium show that the insolubility in water and solubility in organic solvents increase with the molecular complexity of the secondary amine. Salts of amines can be substituted for free amines in this reaction.

MISCELLANEOUS.

British Association for the Advancement of Science.—The Council has nominated Mr. Francis Darwin, F.R.S., Foreign Secretary to the Royal Society, and author of the "Life and Letters of Charles Darwin," to be President of the meeting next year, when for the fourth time in its history the Association will assemble in Dublin. The arrangements for the meeting at Leicester, which will open at the end of next month, under the Presidency of Sir David Gill, K.C.B., F.R.S., formerly Astronomer Royal at the Cape, are now well advanced. A generous measure of local hospitality has been provided, and among other social functions there will be given by the Mayor of Leicester, Alderman Sir Edward Wood, an Evening Fête in the Abbey Park; by the President and Council of the Leicester Literary and Philosophical Society, a Conversazione in the Museum Buildings; and by Sir Samuel and Lady Faire, a Garden Party at Glenfield Frith.

MEETINGS FOR THE WEEK.

Wednesday, 19th.—Microscopical, 8. "Eye-pieces for the Microscope," by E. M. Nelson. "The Life-history of the Tiger Beetle, *Cicindela campestris*" (Illustrated by Lantern Slides), by F. Enock.

Thursday, 20th.—Chemical, 8.30. "Some Properties of Radium Emanation," by A. T. Cameron and Sir W. Ramsay. "Affinity Constants of Amino-sulphonic Acids as Determined by the Aid of Methyl-orange," by V. H. Veley. "Azo-derivatives of 1 : 3-Diphenylbarbituric Acid - Dynamic Isomerism among the Coloured Hydrazones of 1 : 3-Diphenylalloxan," by M. A. Whiteley. "A Series of Coloured Diazo-salts derived from β-Amino-aceto-α-naphthalide," by G. T. Morgan and W. O. Wootton. "Colour and Constitution of Azo-compounds," by J. T. Hewitt and H. V. Mitchell. "Oxidation of Hydrazines by Free Oxygen," by F. D. Chattaway. "Calmatambin, a New Glucoside," by F. L. Pyman. "Decomposition of Hyponitrous Acid in presence of Mineral Acids," by P. C. Ray and A. C. Ganguli. "Chemical Composition of Petroleum from Borneo," by H. O. Jones and H. A. Wootton. "Synthesis of Phenonaphthacridines—Trimethylphenonaphthacridines" and "Condensation of Aldehydes with Mixtures of α-Naphthol and α-Naphthylamine—Synthesis of 7-Aryl-

dinaphthacridines," by A. Senier and P. C. Austin. "Improved Form of Apparatus for the Rapid Estimation of Sulphates and Salts of Barium" and "The Determination of Sugar by Fehling's Solution," by W. R. Lang and T. B. Allen.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2482.

ON THE THERMO-CHEMISTRY OF FLAME SPECTRA AT HIGH TEMPERATURES.*

By W. N. HARTLEY, F.R.S., D.Sc., Royal College of Science Dublin.

(Concluded from p. 279).

The Alkaline Earths.

It has been shown that these substances are of a different nature, and their salts are sharply divided into two classes, the haloid and the oxy-salts, each with a different behaviour.

The Haloid Salts.—These are volatile in flames supplied with the halogen hydrides without decomposition. They are also volatile without decomposition in a dry carbonic oxide flame. Here, then, we may probably have the spectra of salts and not of the metals. In a hydrogen or coal-gas flame the salts are hydrolysed and converted into oxides by heat; this is a fact well known. If we examine the heat of formation of the chlorides, we find it to be, for calcium and strontium respectively—

$$\xi CaCl_2 = 169{\cdot}9\ K^\circ \text{ and } \xi SrCl_2 = 184{\cdot}7\ K^\circ,$$

while the oxides are—

$$\xi CaO = 131{\cdot}5\ K^\circ \text{ and } \xi SrO = 131{\cdot}2\ K^\circ.$$

The barium chloride has not been determined, but the oxide is—

$$\xi BaO = 133{\cdot}4\ K^\circ,$$

(A. Guntz, *Comptes Rendus*, 1903, cxxxvi., 1071), and we may therefore safely say that the energy of formation of the chloride does not differ much from the number deduced from strontium chloride or about 187 K°.

The effect of water-vapour in the flame is an endothermic reaction when the chloride is a solid.

$$\xi(CaCl_2 + H_2O = CaO + 2HCl) = -37{\cdot}5\ K^\circ;$$

and where towards 2000° C.—

$$\xi H_2O = 50{\cdot}6\ K^\circ \text{ and } \xi CaO = 131{\cdot}5\ K^\circ.$$

The corresponding value for $SrCl_2$ is $-52{\cdot}1$ K°. When the chlorides are vaporised in the flame, these endothermic values must be much less, and the reactions are easily reversed, as we know by experience when gaseous hydrochloric acid or much ammonium chloride is passed into the flame. We can see clearly also why it is that the carbonic oxide flame does not decompose these salts, the heat of combination of the chlorides being much in excess of that of the oxides, and the reducing power of carbonic oxide, which is the converse of the energy of formation of carbon dioxide, much less, thus:—

$$\xi(CO + O = CO_2) = 68{\cdot}3\ K^\circ.$$

It is different with cupric chloride, as this in time is reduced to copper.

The Oxy-salts.—These are all resolved into either oxides or sulphides, or mixtures of the two, when heated in the oxyhydrogen flame. The energy of formation of the oxides is as follows:—

$\xi CaO = 131{\cdot}5$ K°, $\xi SnO = 131{\cdot}2$ K°, and $\xi BaO = 133{\cdot}4$ K°, there being very little difference between them, but these values are all below those of lithium and rubidium, where—

$$\xi Li_2O = 141{\cdot}2\ K^\circ \text{ and } \xi Rb_2O = 165{\cdot}4\ K^\circ.$$

We have now to take into consideration the reducing power of hydrogen at high temperatures in flame reactions. There are two values for the production of gaseous water, the smaller of which is at a temperature approaching 2000°, which we may consider to be the highest temperature of all flames capable of melting platinum—

$$\underset{T}{\xi H_2O} = 58{\cdot}1\ K^\circ \text{ and } \xi H_2O = 50{\cdot}6\ K^\circ.$$

The decreasing value at high temperatures is evidence of the dissociation of water-vapour, which we know does occur at the temperature of white-hot platinum. Now both the above values are below that obtained by the combustion of carbon monoxide.

$$\underset{T}{\xi}(\underset{T}{CO} + \underset{T}{O} = \underset{T}{CO_2}) = 68{\cdot}2\ K^\circ;$$

it is therefore unnecessary to consider a coal-gas flame apart from one fed with hydrogen, for many of the reductions and dissociation phenomena that can take place in the latter may occur in the former.

The high temperature tends to the dissociation of other oxides than water, and the alkaline earths are most certainly volatilised in Deville's blowpipe flame, whether they are first dissociated or not. Furthermore, reduction processes are carried on in the solid material, which have not hitherto been suspected, such as the reduction of strontium and barium sulphates to sulphides, and of beryllia and alumina to the state of metal.

In the metallurgical process of zinc distillation, the presence of carbon mixed with the ore is necessary. The energy of formation of zinc oxide is $\xi ZnO = 84{\cdot}8$ K°. Supposing the reduction to take place through the medium of carbon monoxide, we have the following:—

$$\xi(ZnO + C = Zn + CO) = -55{\cdot}4\ K^\circ \quad . \quad . \quad I.$$

$$\underset{84{\cdot}8}{\xi}(ZnO + CO = Zn + \underset{68{\cdot}3}{CO_2}) = -16{\cdot}5\ K^\circ \quad . \quad . \quad II.$$

Endothermic.

In this case we are considering a solid oxide, not one in the state of vapour; nevertheless, we know that reduction does occur though the reaction is endothermic. By recent observations it has been shown that zinc oxide is vaporised at 1400° and rapidly at 1700° C., and this must greatly facilitate the reduction process (see F. O. Doltz and C. A. Grammann, "Metallurgie," 1906, iii., 212, 372).

The reduction of cadmium is more easily accomplished than that of zinc, and hence the cadmium distils over first. The obvious reason for this is that the heat of formation of the oxide is about 21 K° less than that of zinc oxide and $\xi CdO = 65$ K°; we have, then, the following equation:—

$$\xi(CdO + C = Cd + CO) = 3{\cdot}2\ K^\circ.$$

The reduction of cadmium is a feebly exothermic process. Let us take another instance, that of the reduction of a solid oxide such as alumina.

The combination of this with oxygen gives an amount of energy which has not hitherto been measured directly, but the heat of formation of the colloidal hydroxide is known, and it must be accepted as being somewhat greater than that of the oxide, but only slightly greater. It is expressed by the following equation:—

$$\xi(2Al + 3O + xH_2O = Al_2O_3.xH_2O) = 393\ K^\circ.$$

All attempts to reduce alumina by means of carbon alone, or carbon acting jointly with carbon monoxide on an industrial scale, have failed, though many such processes have been devised.

The fact may be accounted for by the following equations:

$$\xi Al_2O_3 = 393\ K^\circ \text{ or } \xi\tfrac{1}{2}Al_2O_3 = 131\ K^\circ \text{ endothermic};$$

$$\xi(2Al_2O_3 + 3C = 4Al + 3CO_2) = -495\ K^\circ.$$

or, for 1 atom of oxygen removed, $-82{\cdot}5$ K°.

Substituting for solid carbon, gaseous hydrogen, we have

$$(\xi\tfrac{1}{2}Al_2O_3 + H_2 = \tfrac{1}{3}Al_2 + H_2O) = -72{\cdot}9\ K^\circ,$$

* A Paper read before the Royal Society, January 31st, 1907. (Revised March 22nd).

not a very great difference. Substituting gaseous carbon monoxide for solid carbon, we obtain—

$$\underset{393}{\xi}(Al_2O_3 + 3CO = 2Al + \underset{68{\cdot}3\times3}{3CO_2}) = -188{\cdot}1\ K^\circ,$$

or, for 1 atom of oxygen removed, $\frac{1}{6}$ of this $= -62{\cdot}7\ K^\circ$.

The actual energy supplied in these reactions before the aluminium can be reduced is for carbon, carbon monoxide, and for hydrogen respectively, $-82{\cdot}5\ K^\circ$, $-62{\cdot}7\ K^\circ$, and $-72{\cdot}9\ K^\circ$. The carbon monoxide value is thus shown to be less than that in either of the other two reactions. It has already been proved, first, that alumina is reduced to the metallic state in the oxyhydrogen flame; secondly, that the reduction takes place more easily when the alumina is mixed with some dense form of carbon. In the first instance, the flame alone supplied hydrogen only as the reducing agent; consequently, the energy required for every atom of oxygen removed was $72{\cdot}9\ K^\circ$ in the form of extraneous heat which was necessary not only for initiating the process, but also maintaining it. When solid carbon was used, this was a somewhat higher figure, being $82{\cdot}5\ K^\circ$, but this very reduction process with solid carbon would result in the formation of carbon monoxide which could then operate upon another molecule of alumina, which places the extreme limits of the energy required for reduction as between $63\ K^\circ$ and $82{\cdot}5\ K^\circ$. From this it would appear that *any reducing process may be carried out in the oxyhydrogen flame by a purely chemical action if the extraneous energy required to initiate and maintain the action does not exceed* $84{\cdot}8\ K^\circ$ *per atom of oxygen to be removed.* (This is the figure for the zinc reduction $\xi ZnO = 84{\cdot}8\ K^\circ$, that calculated for alumina is $82{\cdot}5\ K^\circ$).

Let us now consider another instance of the reduction of a solid oxide in the flame, namely, beryllia. The energy of formation of the oxide is unknown, but its composition is BeO.

Pollok has measured the heat of formation of the chloride $\xi BeCl_2 = 155\ K^\circ$, and of the heat of dissolution of beryllium in aqueous hydrochloric acid $\xi BeCl_2 = 199{\cdot}5\ K^\circ$. Comparing these results with the heat of formation and solution of aluminium chloride, we obtain the following figures:—

	Al_2C_6.	$\frac{2}{3}Al_2Cl_6$.	$BeCl_2$.
Heat of formation ..	323·6	107·9	155·0
Heat of solution . ..	152·6	50·9	44·5

Similar comparisons, made with magnesium and zinc chlorides, give:—

	$BeCl_2$.	$MgCl_2$.	$ZnCl_2$.
Heat of formation ..	155·0	151·0	97·4
Heat of solution . ..	44·5	36·0	15·6

These figures show that in each case a fall in the heat of formation and solution accompanies the rise in the atomic weights.

Now—

$$\xi Al_2O_3 = 393\ K^\circ = \xi\tfrac{2}{3}Al_2O_3 = 131\ K^\circ,$$

and—

$$\xi\tfrac{2}{3}Al_2Cl_3 = 107{\cdot}9\ K^\circ;$$

the difference, $23{\cdot}1\ K^\circ$, shows that the energy of formation of the oxide is by that amount greater than the chloride, and as—

$$\xi BeCl_2 = 155\ K^\circ,$$

we may assume the value—

$$\xi BeO = 178{\cdot}1\ K^\circ$$

to be approximately correct. But—

$$\xi MgO = 143{\cdot}4\ K^\circ \text{ and } \xi ZnO = 84{\cdot}8\ K^\circ,$$

also—

$$\xi MgCl_2 = 151{\cdot}0\ K^\circ \text{ and } \xi ZnCl_2 = 97{\cdot}4\ K^\circ,$$

the difference between magnesium chloride and oxide is $7{\cdot}6\ K^\circ$, and between zinc chloride and oxide $2{\cdot}6\ K^\circ$, we may assume then that $\xi BeO = 148\ K^\circ$, and this number is very probably more correct than that derived from the figures obtained from a comparison of the difference between the oxide and chloride of aluminium, because magnesium and zinc belong to the same group as beryllium, and aluminium does not.

The metal is certainly reduced from the oxide by the oxyhydrogen flame, and as far as we know beryllia is not a volatile oxide, nor is it fusible. The reduction must therefore be the result of a purely chemical action, and it must also be of a highly endothermic character, as may be seen by the equation following:—

$$\underset{148}{\xi}(BeO + H_2 = Be + \underset{50{\cdot}6}{H_2O}) = -97{\cdot}4\ K^\circ.$$

Endothermic.

It may be inferred from the evidence afforded by the flame spectra, that at these high temperatures the infusible and non-volatile metallic oxides are in a peculiarly active condition, having absorbed a large amount of energy from the flame, so that they are approaching the condition of dissociation, and are therefore subject to chemical interactions with the reducing gases, which otherwise would have no power to reduce them. But in the cases referred to, the reducing gas is hydrogen, and in all probability it is not the hydrogen supplied to the flame in the molecular condition, but hydrogen in the atomic or nascent state, resulting perhaps from the dissociation of water, the product of combustion in another part of the flame, which carries with it the additional charge of energy which enables it to initiate and complete the reduction process.

Conclusions.

1. The oxides of calcium, strontium, and barium are not dissociated by heat alone, because they show no spectrum in a carbon monoxide flame. 2. They are reduced by the combined action of heat and hydrogen in the oxyhydrogen flame and by the action of cyanogen in the cyanogen flame. 3. The flame coloration is due to the metal, because not only is the flame spectrum from lime essentially the same as that of the metal calcium, but also the heats of formation of CaO, SrO, and BaO have very nearly the same value, and that where calcium oxide can be reduced the other oxides could, on that account, undergo a similar reduction. Whether the compound of strontium or barium in the flame be a sulphide or an oxide, the same spectrum is emitted, but there is some uncertainty as to whether the barium sulphide is not converted into oxide by water-vapour in the flame.

The explanation given by Lenard, of the flame coloration by the alkali salts, appears to be inapplicable to the coloration of the carbon monoxide flame by the haloid salts of the alkaline earth metals.

Spectroscopic Apparatus.—Messrs. Adam Hilger, Ltd., have sent their latest catalogue of "Spectroscopes and Spectroscopic Apparatus." It is evident that great advance has been made in the design and manufacture of these instruments, particularly in those adapted to the production of photographic records. Quartz lenses and prisms are used, the latter being cut on the "Cornu" plan, in two halves, one right and the other left-handed, so as to avoid double refraction. By using Wratten and Wainwright's panchromatic plates with these instruments it is possible to get photographed spectra from λ 2000 down to λ 7000. The value of such apparatus in experimental research is so obvious that the wonder is we have had to wait so long for them. We have seen a print of the copper spectrum made on their smallest quartz instrument and enlarged three and a-half times; the lines are clear and sharp from one end to the other, and testify to the excellence of the workmanship. Messrs. Hilger have also two models of photo-measuring micrometers designed for use with spectrum photographs, together with many other forms of spectroscopic apparatus now coming into general use, including Appleyard's Spectroscope-refractometer, Michelson's Interferometer, and Lummer Gehrcke's Parallel Plate Spectroscope.

INFLUENCE OF SOLVENTS IN THE CLAISEN CONDENSATION.

CATALYTIC ACTION OF ETHER AND OF TERTIARY BASES IN THIS REACTION AND ALSO IN THE FORMATION OF THE GRIGNARD REAGENT.

(Preliminary Communication).

By J. BISHOP TINGLE and ERNEST E. GORSLINE.

In a paper read in abstract before the American Chemical Society, at the New York meeting in December, 1906, we stated that we had obtained evidence which pointed to a specific action on the part of the solvent on the course of the Claisen condensation. We have now accumulated a number of observations bearing on this subject, all of which point to the *complete parallelism of the Claisen and Grignard reactions, so far as the effect of solvent is concerned.* We find that certain reactions, such for example as that between ethyl oxalate and camphor, take place readily and, apparently, with practically equal ease in ligroin or in ether solution. Others, such as that between ethyl phthalate and camphor, require many hours or days in ligroin solution, but take place easily when the materials are dissolved in ether. If a litttle ether be added to the ligroin solution, reaction begins at once and proceeds to completion. Apparently, the time required to carry the reaction to an end is dependent, other things being equal, on the amount of ether added. The position, then, is this, *we can accelerate or retard a given condensation by adding or withholding ether from the solution.*

The questiou at once arises, is this change in the velocity of the reaction due to a difference in the solvent action of the ether, or ether-ligroin mixture, as compared with the ligroin alone, or is it due to a difference of the temperature at which the reactions were carried out? With regard to the last point we may say that all our ligroin boiled at 36°, so that experiments carried out at its boiling point were practically at the same temperature as those carried out at the boiling point of ether. Actually, however, the majority of the experiments were performed at the temperature of the room. Moreover, we find that, under otherwise similar conditions, the time and temperature factors are inversely proportional, *i.e.*, a reaction which requires days for completion at the ordinary temperature, will be finished in a few hours if the temperature is raised to that of the boiling point of the solvent. The yield of the condensation product is practically the same in the two cases. In all our experiments, unless otherwise stated, we used sodium wire as the condensing agent. It is, perhaps, hardly necessary to add that, before use, all our solvents were treated with sodium wire until they ceased to react with it.

We may now take up the question of the solvent action of ether and ligroin. Camphor and all of the esters we employed dissolve in each solvent with great and, apparently, equal readiness, and the same is true of the condensation products; consequently the difference of solubility, if it exists, must be concerned with the sodium salts formed during the condensation of the ketone and ester. We have paid a good deal of attention to this point and have observed that the substances formed on the sodium wire sometimes flake off as rapidly as they are produced, and become partly suspended and partly dissolved in the liquid; often there is a deposit of this material on the bottom of the flask; frequently, however, it is all, or practically all, in solution. Sometimes the sodium wire becomes thickly incrusted with a hard, rough coating of a salt, which clings to the metal and retains the general shape of the original wire. Contrary to our expectations, the formation of this substance does not materially protect the sodium from being attacked by the reagents, nor does it adversely affect the yield of condensation product. Examination of the incrusted material will show that it often contains a minute thread of metal.

These differences appear to depend upon extremely subtle changes in temperature, speed of reaction, &c., and it is impossible for us to define exactly the conditions necessary for obtaining any given result, though all of them will be observed if a considerable number of condensations is carried out. In some instances, moreover, the sodium salt formed remains incrusted over the wire and retains the wire form when examination shows that all the sodium has disappeared. The interesting point in this connection is that the *yield of condensation product is essentially the same whether the sodium compound dissolves in the liquid, is suspended in it, or forms a crust over the sodium wire.* In order to cast a little additional light on the subject we prepared a concentrated solution of sodium ethylate in alcohol. Equal volumes of ether, ligroin, benzene, and toluene were mixed with separate, equal quantities of this alcoholic solution; in no case was a precipitate or turbidity formed. As is well known, sodium ethylate free from alcohol is practically insoluble in ether or ligroin, but this fact has no direct bearing on our experiments. Having now determined the influence of all the factors which we thought likely to affect the result, and having established, thereby, the specific action of ether as an accelerator of the condensation, we turned our attention to the discovery of other substances which might exert a similar influence. Two of these we found to be pyridine and quinoline, which appear to be about equal in their efficiency. Their influence is quite well defined, though it is not as great as that of ether. We have carried out experiments in ligroin solution, adding a little of each tertiary base, and have also made condensations with pyridine alone as the solvent. The results were similar in all cases. Furthermore, we believe that we have evidence showing that, in the case of condensation compounds capable of existing in both the enolic and the ketonic forms, the use of pyridine or quinoline in the course of their formation leads to a disturbance of the ordinary equilibrium in favour of the production of the ketonic form. This is one of the points which is, at present, under investigation; should it prove to be substantiated we may expect that it will be of considerable importance in the preparation of the class of bodies in question.

One of the theories regarding the course of the Claisen condensation postulates the formation of sodium ethylate as the first step; this is supposed to undergo certain changes, resulting, finally, in the elimination of 2 molecules of alcohol for each molecule of sodium ethylate added. In this manner it has been sought to explain the gradual acceleration of the reaction leading to the production of ethyl acetoacetate. Should this hypothesis be correct it is evident that sodium ethylate itself should be an excellent accelerator. This we have found to be the case. The addition of a few drops of absolute alcohol, saturated with sodium, to a mixture of ligroin, ethyl acetate, and sodium wire immediately starts a reaction. A comparison experiment showed that alcohol itself assisted in promoting the action of the sodium, to an extent even greater than that exhibited by sodium ethylate. In presence of the latter the sodium wire was immediately darkened and the reaction continued steadily to the end. With the absolute alcohol the sodium wire remained entirely unattacked for nearly five minutes; a white compound was then formed in small quantity, and immediately thereafter a darker coloured product. The reaction now proceeded rapidly and was apparently completed much sooner than when sodium ethylate was used. These experiments were carried out with camphor and ethyl phthalate, in ligroin solution. It may be added that in the course of a large number of experiments performed with various esters and condensing agents, we have never obtained a good yield of condensation product if we found it necessary to add alcohol in order to bring the sodium into solution. This is in entire accord with Claisen's experience. He found that sodium ethylate, in alcoholic solution, was the least active

condensing agent. This point is at present under investigation.

In a series of papers of great interest, W. Tschelinzeff (*Ber.*, 1905, xxxvii., 2081, 4534; xxxviii., 3664; *cf.* Tingle, *Amer. Chem. Journ.*, 1906, xxxv., 94) has shown that the Grignard reagent is probably an oxonium derivative, that at all events, as usually prepared, it contains ether as an integral part of the molecule. He has also demonstrated that certain tertiary bases, such as dimethylaniline, can take the place of the ether, and, further, that although, in the absence of ether or of a tertiary base, the formation of the Grignard reagent does not take place at the temperature of boiling ether, yet it does so if the temperature be sufficiently raised, say to that of boiling benzene or toluene. He points out that both the ether and tertiary base act as typical catalytic agents in this reaction, and give the formulæ—

$$(C_2H_5)_2O\lessgtr^{X}_{MgR} \quad \text{and} \quad C_6H_5N(CH_3)_2\lessgtr^{X}_{MgR}$$

as representing the probable constitution of the MgR ether compound and that of the tertiary base, respectively. It is at once evident that there is a close analogy between our results with the Claisen reaction and those of Tschelinzeff with the Grignard reagent. Accordingly, we have carried out a number of experiments to clear up certain points regarding which information was not available.

Our conclusions may be briefly summarised as follows :— The rapidity with which the magnesium is attacked by the halide compound is dependent on the nature of the alkyl or aryl halide employed, provided, of course, that other conditions remain constant. The presence of ether is not essential to the reaction, *neither is a high temperature necessary, provided that sufficient time be allowed.* A number of our experiments were carried out at the ordinary room temperature, in ligroin solution (b. p. 36°). The Grignard reaction admits of being controlled with the greatest ease; as is well known, its velocity can be increased by the use of ether, a tertiary base (pyridine, quinoline, &c.), or iodine, or by means of a high temperature (see above). The use of low-boiling ligroin, on the other hand, quickly diminishes the speed of reaction. In short, then, we appear to have a *complete analogy in behaviour between the Claisen reaction and the formation of the Grignard reagent.*

As regards the theory of the latter, we should like to offer a few remarks which will follow the same general lines as the ideas of Tschelinzeff, although there are one or two points which we think are not made quite clear in his paper. The reaction $Mg+RX \rightarrow Mg\lessgtr^{R}_{X}$ takes place with more or less difficulty, depending on the factors referred to above. Grignard's reagent has the formula $Mg\lessgtr^{R}_{X}$, *i.e.*, ether is *not* an essential constituent. The reaction represented above is greatly accelerated by the presence of a little ether, which acts as a catalyst, forming an oxonium compound, such as $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O\lessgtr^{MgR}_{X}$ (Tschelinzeff). Evidently, however, this is *not* the compound which *necessarily* reacts with the aldehyde, ester, &c., in the Grignard condensations; although, of course, in presence of excess of ether it might be capable of doing so, it must therefore be an intermediate compound, in equilibrium, as represented by the equation—

$$Mg+RX+(C_2H_5)_2O \rightleftarrows \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O\lessgtr^{MgR}_{X} \rightleftarrows (C_2H_5)_2O+Mg\lessgtr^{R}_{X}.$$

The question now arises—To what is the acceleration of the ether due? As it is difficult to see how it can have any effect on the magnesium metal, we can only regard it as favouring the dissociation of the alkyl halide into R + X, and since the question is not one of dilution, we see no escape from the conclusion that it forms the oxonium compound, $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O\lessgtr^{R}_{X}$, which would certainly be unstable, and would therefore in all probability unite quickly with the magnesium to form $Mg\lessgtr^{R}_{X}$. In support of this theory of ours we may point out that the corresponding reaction with a tertiary base, leading—in the case of dimethylaniline — to the production of the compound—

$$C_6H_5\overset{R}{\underset{X}{N}}(CH_3)_2$$

is exactly what we expect from such substances, whereas, to say the least, a compound—

$$C_6H_5\overset{MgR}{\underset{X}{N}}(CH_3)_2,$$

as formulated by Tschelinzeff, is very unusual, and without any special analogy. A further point for consideration is the effect of the trace of iodine which is so frequently added to start the attack on the magnesium. In view of the work of Baeyer and Villiger (*Ber.*, 1903, xxxvi., 2775; *cf.* Tingle, *Am. Chem. Journ.*, 1906, xxxv., 95), it can hardly be doubted that a magnesium subiodide, such as Mg_2I_2, is first produced, and that this then reacts with the oxonium compound formulated above. Of course the magnesium is often attacked directly by the halide compound; to what extent this occurs obviously depends on the nature of the latter. To sum up, then, we regard the acceleration in the formation of the Grignard reagent as dependent on such actions as are represented by the equations :—

1. $Mg+I_2 \rightarrow IMg.MgI.$
2. $RX+(C_2H_5)_2O \rightleftarrows \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O\lessgtr^{R}_{X}.$
3. $\begin{matrix}(C_2H_5)_2O\\(C_2H_5)_2O\end{matrix}\!\!>\!\overset{R+MgI}{\underset{X}{\underset{X}{\;}}} \rightarrow 2(C_2H_5)_2O+X_2+2RMgI.$

Almost ever since the discovery of ethyl acetoacetate the mechanism of its formation has been a matter of controversy. The investigation of the Claisen condensation, of which the reaction in question is a special case, so far from settling the matter, appeared to rouse the combatants to greater efforts and more vigorous language. During the past ten years the dispute has been carried on chiefly by Claisen, Michael, and Nef, each of whom had a particular theory to support. Quite recently Professor Nef (*Amer. Chem. Journ.*, 1907, xxxvii., 302) has announced that he has abandoned his own theory in favour of that of Claisen. It is but just to say that he is, apparently, at present, at least as emphatically in favour of Claisen's theory as, heretofore, he has been against it, and that now he appears to be just as certain that Claisen is right and Michael is wrong as, in the past, he has been prepared to demonstrate, beyond question, that they were both absolutely in error. To us, and we believe to most chemists, the only thing about the matter which is beyond dispute is that when three investigators of the eminence of Messrs. Claisen, Michael, and Nef disagree on a question, it may be taken

as certain that the experimental data are necessarily inadequate to support any theory.

It would be easy for us to put forward a more or less attractive looking scheme of equations which could be made to include many fanciful dissociations and be in accord with our own work; we have not done so because we believe that such an attempt is premature in the present state of knowledge of the subject. Nevertheless, we desire to emphasise the fact that any hypothesis which may be put forward in the future will have to take account of the *accelerating action of ether and of the tertiary bases, and also of the similarity between the Claisen reaction and the formation of the Grignard reagent.*

Experimental.

The following experiments were carried out with camphor (1·5 mol.), unless otherwise stated. The proportion of sodium wire was 1 atom and of the particular ester 1 molecule.

1. No apparent action takes place on adding camphor, dissolved in ethyl benzoate, to sodium dissolved in absolute alcohol (4 mol.). After remaining for some hours the mixture was heated on the water-bath for two hours. A light colored precipitate formed which gradually settled as a dark cake on the bottom of the vessel. Treatment with ice water followed by acidification gave unchanged ethyl benzoate. No condensation compound could be detected. This experiment shows how *slight* is the *condensing power of sodium ethylate*: the following two demonstrate the *effect of temperature.*

2. Ethyl benzoate and camphor, with sodium wire and ligroin (b. p. 36°), were mixed at the ordinary room temperature. After forty-eight hours, without heating, the sodium had almost entirely disappeared. In another experiment the time required was five working days.

3. In this experiment the mixture was heated on the water-bath to the boiling point of the solvent. After two hours action appeared to be complete, but the mixture was allowed to remain over night. The yield was practically the same as in 2.

Experiment 4 proves the effect of *differences in the ester.*

4. Ethyl oxalate, under conditions given in 2, reacts vigorously in a few minutes, without external heat. The yield was essentially the same as usual (*vide* Bishop Tingle; *Amer. Chem. Journ.* 1897., xix, 393; 1898, xx., 218).

The result of differences in the *constitution of the ketone or aldehyde* employed is sufficiently evident from Claisen's work, so that we paid no particular attention to this point.

Our next experiments were directed to prove that *the solvent* exercises a *decided effect on the progress of the reaction.*

5. Experiment 2 was repeated, except that to the 400 cc. of ligroin 100 cc. of absolute ether were added. The wire quickly darkened and became rough, and a dark mass collected at the bottom of the vessel. At the end of three hours, without heating, the action was complete and an excellent yield of condensation product was obtained. This, taken in conjunction with the second experiment, not only proves the question of acceleration, but also shows that the action is *not due* to *increased solubility* of any sodium salt in the ether-ligroin mixture, as compared with ligroin alone.

Experiments 6 and 7 demonstrate the result of the addition of *pyridine* and *quinoline*, respectively, in place of ether.

6. The conditions were similar to Expt. 5, but 75 cc. of pyridine were added in place of the ether. The liquid rapidly darkened and behaved essentially as in the previous case. The reaction appeared to be complete in about twelve hours. The yield was poor.

7. In this case the pyridine was substituted by 20 cc. of quinoline. Action commenced at once, the liquid depositing a dark brown substance in the usual manner. The mixture was heated to boiling for two hours, at the end of which time the action was finished. The yield was good.

The influence of *sodium ethylate* or of *absolute alcohol, in small quantity*, is shown by Expts. 8 and 9.

8. Experiment 7 was repeated, but in place of the quinoline there was added 50 cc. of absolute alcohol saturated with sodium ethylate, *i.e.* treated, with the metal until the latter remained undissolved. The liquid darkened at once, the wire became coated, and after ten minutes the contents of the flask began to boil quietly. After thirty minutes the wire had completely disintegrated. The yield of condensation product was very poor, but a relatively large quantity of benzoic acid was obtained.

9. This was essentially the same as Expt. 8, except that for the sodium ethylate solution there was substituted an equal volume of absolute alcohol. The action was complete in fifteen minutes, and, as in the previous case, a red mass settled to the bottom of the vessel.

We have carried out experiments with camphor and ethyl phthalate similar to Expts. 2, 5, 7, 8, and 9 recorded above for ethyl benzoate. In general, the results were entirely analogous; the chief difference is that ethyl phthalate reacts rather more readily than ethyl benzoate. In a further experiment we tried the effect of adding 2 drops of sodium ethylate solution, as above, to the substances dissolved in 200 cc. of ligroin. The reaction was, of course, not so rapid as in those experiments where a larger quantity was added, but its accelerating action was more marked than that of 10 cc. of quinoline or or 25 cc. of ether, under similar conditions. The yield was, however, *markedly less*, only about half of that obtained by the use of ether or of quinoline, or when no accelerator is employed.

We have also studied the condensation of ethyl acetate to ethyl acetoacetate. By dissolving the ester (17·6 grms.) in ligroin (b. p. 36°, 200 cc.) and adding the sodium wire, the reaction proceeds very slowly and was not completed after six hours' boiling; indeed, some wire remained undissolved after five days' subsequent standing, at the ordinary temperature. In contrast with this the addition of 75 cc. of ether caused the disappearance of the sodium after two hours' heating. Pyridine (50 cc.) acted in almost exactly the same way. The use of 5 drops of sodium ethylate solution once more demonstrated how rapidly this substance stimulates a reaction. After 0·5 hour at the ordinary temperature and one hour's heating, the sodium had nearly all dissolved. The ethyl acetoacetate was separated and identified in the usual manner, by the ferric chloride test and by fractionation under reduced pressure.

Experiments on Grignard's Reaction.

Ethyl chloracetate, in ethereal solution, reacts very vigorously with magnesium. In ligroin (b. p. 36°) solution, on the other hand, no change was apparent after three hours' boiling. The addition of a fragment of iodine, followed by boiling for ten hours, caused the production of a quantity of light yellow material. The experiment was repeated, 10 cc. of ether being used in addition to the ligroin. There was no change after three hours' boiling, but when a fragment of iodine was added a rather vigorous action began, the light yellow solid collecting in fairly considerable quantity. This demonstrates the *formation of Grignard's reaction at* 36°.

Experiments were now carried out with ethyl iodide (7·8 grms.), magnesium (1·22 grms.), ligroin (500 cc.) and quinoline (30 cc.). There was no evident action on standing at the ordinary room temperature, but the magnesium was almost completely dissolved after boiling during twenty minutes. The experiment was repeated, ether (25 cc.) being substituted for the quinoline. In this case the reaction began vigorously in the cold and the liquid soon commenced to boil.

Further experiments were carried out with pyridine in

the place of quinoline, the results being essentially similar to those described above.

Our work is being continued in several directions and we hope to communicate further results, together with fuller experimental details, in a subsequent paper.—*American Chemical Journal*, xxxvii., No. 5.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART II.—ANALYSIS OF THE SILVER, COPPER, AND TIN GROUPS.

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Continued from p. 282).

CONFIRMATORY EXPERIMENTS AND REFERENCES (*contd.*).

Analysis of the Copper Group.

P. 23, N. 1: *Solubility of the Copper Group Sulphides in* HNO_3.—500 mgrms. of Pb, Bi, Cu, and Cd as sulphides were treated in separate experiments according to P. 23; the sulphides dissolved almost completely when the solution began to boil, but the sulphur residue remained dark coloured (except in the case of cadmium) even after several minutes' boiling.

500 mgrms. Pb, Bi, Cu, and Cd as sulphides were in separate experiments boiled in an open casserole with about 30 cc. of a mixture of one volume HNO_3 (1·20) and three volumes of water; Bi_2S_3 and CuS dissolved in five minutes or less, PbS dissolved less readily, and CdS only after ten to fifteen minutes. The experiment was repeated, except that 50 cc. of a still more dilute acid was used; the result was the same, except that solution took place somewhat less rapidly.

500 mgrms. Hg as HgS were treated according to P. 23; and the filtrate was evaporated with excess of HCl to a small volume, diluted, and saturated with H_2S; a precipitate of HgS estimated to contain less than 1 mgrm. Hg resulted. The experiment was repeated, except that 30 cc. HNO_3 (1·20) were used, and the boiling continued for ten minutes; a precipitate of HgS estimated to contain 2 mgrms. Hg resulted. The experiment was repeated, except that 30 cc. of a mixture of one volume of HNO_3 (1·20) and three volumes of water were used, and the boiling continued for ten minutes; a precipitate of HgS containing about 0·5 mgrm. Hg was formed. One mgrm. Hg as HgS was boiled with HNO_3 (1·20) for ten minutes; no change in the amount of the sulphide was apparent.

P. 23, N. 4: *Action of Strong* HNO_3 *on* HgS.—500 mgrms. Hg as HgS were boiled for ten minutes with 30 cc. HNO_3 (1·42); the black precipitate had then become pure white. The filtrate was freed from HNO_3 and saturated with H_2S; a precipitate containing several mgrms. Hg was formed. The experiment was repeated, replacing the HNO_3 (1·42) by the strength used in P. 23; no change in the appearence of the precipitate took place.

P. 23, N. 5: *Action of Dilute* HNO_3 *on* Au *and* PtS_2.—That small quantities of gold and platinum are not dissolved in P. 23 is shown by the results of Test Analyses, Nos. 106 to 113.

P. 23, N. 6: *Oxidation of* PbS *to* $PbSO_4$.—500 mgrms. Pb as freshly precipitated PbS were treated according to P. 23, and to the filtrate $BaCl_2$ was added in large quantity; a precipitate of $BaSO_4$ estimated to correspond to 20 to 30 mgrms. Pb was formed. The experiment was repeated, except that the sulphide was boiled for ten minutes with a more dilute acid, containing one volume HNO_3 (1·20) and three volumes water; the result was the same. The experiment was repeated, except that HNO_3 (1·20) was used, and the mixture boiled for ten minutes; there was left with the sulphur a small white residue of $PbSO_4$, estimated to contain 5 mgrms. Pb, showing that the amount of H_2SO_4 formed increases with the HNO_3 concentration.

Solubility of $PbSO_4$ *in Dilute* HNO_3.—To 50 and 100 mgrms. Pb as $PbSO_4$ in separate experiments 30 cc. of a mixture of one volume HNO_3 (1·20), and three volumes of water were added, and the mixtures heated; the 50 mgrms. dissolved in the cold, the 100 mgrms. upon boiling.

P. 23, N. 7: *Action of* HNO_3 *on* SnS, SnS_2, *and* Sb_2S_3.—Ten mgrms. Sn as SnS and 10 mgrms. Sn as SnS_2 were in separate experiments treated by P. 23; there was a white residue in each case. The filtrate was evaporated with H_2SO_4 to slight fuming, diluted, and saturated with H_2S; a yellow precipitate of SnS_2 estimated to contain 0·5 mgrm. Sn was formed.

Ten mgrms. Sb as freshly precipitated Sb_2S_3 were treated by P. 23; the orange colour of the sulphides disappeared at once, and a small white precipitate separated, which was estimated to contain 3 to 4 mgrms. Sb. The experiment was repeated with 5 mgrms. Sb; no white residue was left. The filtrates in these two experiments were made alkaline with NH_4OH; no precipitate of antimony hydroxide separated, even on standing.

P. 24, N. 1: *Behaviour of* HgS, PtS_2, Au, *and Metastannic Acid towards Bromine Solution.*—100 mgrms. Hg and 500 mgrms. Hg as precipitated HgS were warmed slightly in a covered casserole with 30 to 40 cc. saturated Br_2 solution; the 100 mgrms. dissolved completely, and about three-fourths of the 500 mgrms. dissolved. The latter was treated with another portion of bromine water; the residue became nearly white, but blackened slightly when treated with ammonium sulphide.

The experiment was repeated with 10 mgrms. Sn as metastannic acid, obtained by treating SnS with dilute HNO_3 by P. 23, the solution was boiled, filtered, and saturated with H_2S; scarcely any precipitate of SnS_2 was formed. That even small quantities of Au and PtS_2 dissolve in bromine solution is shown by the results of Test Analyses, Nos. 106 to 113.

P. 24, N. 2: *Reduction of* Hg_2Cl_2 *by* $SnCl_2$.—To 1 mgrm. Hg as $HgCl_2$ in 20 cc. water one drop $SnCl_2$ solution (1 per cent Sn) was added; a nearly white precipitate formed at once. One or two drops more $SnCl_2$ were added; the precipitate darkened rapidly. The experiment was repeated, except that 0·3 to 0·5 cc. HCl (1·12) was added to the $HgCl_2$ solution before the $SnCl_2$; a precipitate formed, which remained white for some minutes, even after the addition of several drops of $SnCl_2$ solution.

P. 24, N. 3: *Oxidation of Mercurous Salts by* HNO_3.—See Part I., C. E., P. 3, N. 7.

P. 24, N. 4: *Colour of Dilute Solutions of Gold and Platinum.*—One mgrm. Au as $AuCl_3$ and 1 mgrm. Pt as H_2PtCl_6 were added in separate experiments to 20 cc. water, and boiled; the solutions had a very pale yellow colour, but this colour was distinct. A few drops of bromine water were added, and the solutions were boiled to expel the bromine; the yellow colour was more distinct than before.

*P. 24*a, N. 1: *Detection of Gold, Platinum, and Mercury in the presence of each Other.*—Mixtures of elements as shown below dissolved in a little dilute HCl were treated by *P. 24*a, and the tests, recorded as in the Test Analyses, resulted as follows:—

Pt	0 —	0 —	1 S	50 S
Au	10 S	1 S	1 S	0 —
Hg	1 S	200 S	200 —	1 S

P. 25, N. 1: *Separation of Metastannic Acid from* HgS.—See Test Analyses, Nos. 10 to 20.

P. 26, N. 1: *Solubility of* $PbSO_4$ *in Water and* H_2SO_4.—According to Bottger (*Zeit. Phys. Chem.*, 1903, xlvi., 604), 10 cc. of the saturated solution in water at 25° contain about 0·3 mgrm. Pb. For its solubility in concentrated H_2SO_4 of different strengths, see Comey, "Dictionary of Solubilities," p. 436.

To determine at what concentration of H_2SO_4 the pre-

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cipitation was nearly complete, several 2 mgrm. portions of Pb as $Pb(NO_3)_2$ were evaporated to fuming with 5 cc. H_2SO_4 (1·84), and the clear solutions obtained were poured into varying amounts of water; the mixtures were cooled, shaken, allowed to stand for a few minutes, filtered, made alkaline with NH_4OH, and treated with H_2S; with 10, 15, and 20 cc. water, the final alkaline solution remained almost colourless when treated with H_2S, thus showing that the amount of lead remaining in the filtrate was scarcely appreciable; when as much water as 50 cc. was used, the liquid was much darkened by H_2S, and a small precipitate of PbS separated on standing.

Influence of HNO_3 on the Solubility of $PbSO_4$.—See C. E., P. 23, N. 6.

To each of several solutions containing 1 mgrm. Pb as $Pb(NO_3)_2$ in 5 cc. HNO_3 (1·20) and 15 cc. water were added 2 cc. of H_2SO_4 (1·84); the mixture was shaken violently, and allowed to stand; only in one or two cases did a precipitate of $PbSO_4$ separate within ten minutes. Three cc. more H_2SO_4 were then added to the solutions that remained clear; $PbSO_4$ precipitated in every case. The experiment was repeated, except that 2 mgrms. Pb were taken; a precipitate of $PbSO_4$ separated when the 2 cc. H_2SO_4 were added. To 1 or 2 mgrms. Pb in 10 cc. HNO_3 (1·20) and 10 cc. water 2 cc. H_2SO_4 were added; no precipitate resulted. Three cc. H_2SO_4 more were added; when 2 mgrms. Pb were present, a precipitate formed. The last experiment was repeated with 4 mgrms. Pb, using 2 cc. H_2SO_4 (1·84); a precipitate of $PbSO_4$ separated.

P. 26, N. 2: *Separation of Bismuth from H_2SO_4 Solutions.*—500 mgrms. Bi as nitrate were evaporated to fuming with 5 cc. H_2SO_4 (1·84), and cooled; a large quantity of a white solid separated. The mixture was added to 20 cc. cold water, and cooled; almost all dissolved, only a very small white residue (2 to 3 mgrms.) being left, which was proved by P. 14 not to be $PbSO_4$; but on standing overnight a large coarsely crystalline white precipitate (probably bismuth oxysulphate) separated. This was filtered off, and the filtrate made alkaline with NH_4OH; a precipitate estimated to contain 40 to 80 mgrms. Bi separated. In another experiment the filtrate, instead of being treated with NH_4OH, was diluted with two volumes of water, and allowed to stand; more of the precipitate separated slowly. The experiment was repeated, except that the clear solution obtained on dilution with cold water was heated to boiling; a large white precipitate separated at once, which was similar in appearance to that obtained in the former experiment; this did not dissolve when the solution was cooled and shaken. Separate portions of the white precipitates which had separated in the preceding experiments from the dilute H_2SO_4 solution on standing, and on heating were treated with 30 to 40 cc. cold H_2SO_4 (1·20); the precipitates dissolved only slightly, even on standing. The undissolved precipitates still containing about 300 mgrms. Bi were collected on filters, and about 10 cc. HCl (1·12) poured over each; clear solutions were quickly obtained.

P. 27, N. 1: *Non-precipitation of Small Quantities of Antimony by NH_4OH.*—Compare C. E., P. 23, N. 7.

Ten mgrms. Sb as $SbCl_3$ and 2 cc. H_2SO_4 (1·84) were added to 10 cc. water; the mixture was evaporated to fuming, cooled, diluted to 15 cc., made just alkaline with NH_4OH, and allowed to stand for thirty minutes; no precipitate separated; but when 10 cc. more NH_4OH (0·96) were added, a very slight white precipitate separated. The experiment was repeated, except that the $SbCl_3$ solution was first warmed with $HCl + HNO_3$ to convert it into the antimonic state; no precipitate separated from the NH_4OH solution, even on standing.

P. 27, N. 2: *Complex Copper-ammonia and Cadmium-ammonia Cations.*—See Dawson and McCrae (*Journ. Chem. Soc.*, 1900, lxxvii., 1239); Euler (*Ber.*, 1903, xxxvi., 3400); Bonsdorff (*Zeit. Anorg. Chem.*, 1904, lxi., 132); Locke and Forssell, (*Am. Chem. Journ.*, 1904, xxxi., 268).

P. 28, N. 1: *Precipitation of* BiOCl.—To 0·25 cc. HCl (1·20) was added 1 mgrm. Bi as chloride, and the solution poured into 100 cc. water at 60°; a precipitate of BiOCl appeared in about a minute. After five minutes the solution was filtered, made alkaline with NH_4OH, and treated with H_2S; no precipitate formed. The experiment was repeated, using 0·5 cc. HCl (1·20) instead of 0·25 cc.; no precipitate of BiOCl formed in five minutes. It was again repeated, using 0·5 cc. HCl and 2 mgrms. Bi; a precipitate of Bi had formed after five minutes, but the filtrate also gave a precipitate with H_2S. It was again repeated, using 1 cc. HCl (1·20) and 6 and 8 mgrms. Bi; with 8 mgrms. Bi a precipitate formed, but not with 6 mgrms.

In a number of experiments 1 mgrm. Bi dissolved in 0·25 cc. HCl (1·20) was poured into 100 cc. water at various temperatures; a precipitate of BiOCl appeared in less than one minute when the temperature was 55°, 70°, 80°, or 90°, in about two minutes at 45°, in about five minutes at 25°, and only after ten to fifteen minutes at 15°.

P. 28, N. 2: *Decomposition of Sodium Stannite Solution.*—A sodium stannite solution was prepared as directed and kept in a stoppered bottle for a week; a black crystalline deposit appeared at the bottom of the bottle.

P. 28, N. 3: *Action of Sodium Stannite on* BiOCl.—Vanino and Treubert (*Ber.*, 1898, xxxi., 1113) have shown that the black precipitate formed by the action of a stannite solution is metallic bismuth, and not BiO, as was formerly supposed to be the case.

0·5 mgrm. Bi as $BiCl_3$ was added in one experiment to 100 cc. water, and in a second one to 500 cc. water; the precipitate formed (which was scarcely visible in the second case) was collected on a filter, washed with water, and then treated with Na_2SnO_2; the greater part of the filter was at once blackened.

Ten mgrms. Pb as $Pb(OH)_2$ were treated on a filter first with a cold Na_2SnO_2 solution, and then with a solution at about 60°; in the first case no blackening occurred in several minutes, while in the second it occurred almost immediately.

The experiment was repeated with 20 mgrms. Sb as antimonous, and with 20 mgrms. Sb as antimonic hydroxide; no blackening was observed in either case.

The experiment with cold Na_2SnO_2 was repeated with 2 mgrms. Fe as $Fe(OH)_3$; the red precipitate did not change colour in ten minutes, but, when hot Na_2SnO_2 was poured over it, it slowly became darker.

P. 29, N. 1: *Precipitation of Copper Ferrocyanide in the presence of a Cadmium Salt.*—A solution containing 1 mgrm. Cu as $CuSO_4$, 500 mgrms. Cd as $Cd(NO_3)_2$, and 2 cc. H_2SO_4 (1·84) was made alkaline with NH_4OH; the solution remained colourless. One-fourth of the solution (about 10 cc.) was acidified with acetic acid, and two drops of a 4 per cent $K_4Fe(CN)_6$ solution added; a white precipitate separated, which had at first only a slight pink tinge, but this colour deepened, and was very apparent after ten minutes. Excess of $K_4Fe(CN)_6$ was then added; much more of the white precipitate separated, and the pink colour of the copper salt was almost obscured. The experiment was repeated, except that only 0·5 mgrm. Cu was taken; the result was exactly the same, thus showing that this test is a very delicate one, provided only two to three drops of $K_4Fe(CN)_6$ solution are first added.

P. 29, N. 2: *Precipitation of Molybdenum by Potassium Ferrocyanide.*—One and 100 mgrms. Mo as MoO_3, and 1 and 10 mgrms. U as $UO_2(C_2H_3O_2)_2$, in separate experiments were dissolved in 2 cc. NH_4OH (0·96), the solutions made acid with acetic acid, and several drops of $K_4Fe(CN)_6$ solution added; no change was observed. The experiments were repeated, except that the NH_4OH solution was acidified with HCl instead of with acetic acid; with the 100 mgrms. Mo and the 10 mgrms. U a large dark red precipitate separated at once; with the 1 mgrm. portions a deep red solution was obtained, from which a dark red precipitate separated after a minute or two.

P. 30, N. 1 and 2: *Complex Cuprocyanide and Cadmicyanide Anions.*—See Euler (*Ber.*, 1903, xxxvi., 3404); Bodländer (*Ber.*, 1903, xxxvi., 3933).

P. 30, N. 3: *Behaviour of Mercury, Lead, and Bismuth in the Cadmium Test with* H_2S.—One mgrm. Hg, 1 mgrm.

Pb, and 1 mgrm. Bi were treated in separate experiments by P. 26, 27, and 30, filtering immediately after the addition of H_2SO_4 and of NH_4OH; there resulted a precipitate with H_2SO_4 in the case of lead and with NH_4OH in the case of bismuth, but none in the case of mercury with these reagents. With H_2S in the KCN solution small dark brown precipitates formed in the lead solution and in the mercury solution, and a very small black one in the bismuth solution. The experiment was repeated with 150 mgrms. Pb and with 150 mgrms. Bi, the precipitates of $PbSO_4$ and of $(BiO)_2SO_4$ and $Bi(OH)_3$ being filtered after cooling and standing a few minutes; even less precipitate resulted in each case than when only 1 mgrm. was used.

Separation of CdS *from Black Sulphides by Dilute* H_2SO_4.—One mgrm. Cd as CdS, freshly precipitated by H_2S from an NH_4OH solution, was boiled gently for about five minutes with 20 cc. of a mixture of one volume of H_2SO_4 (1·20) with four volumes of water; the solution was filtered, diluted with two to three times its volume of water, and saturated with H_2S in the cold; a yellow precipitate of CdS separated.

The experiment was repeated, except that in separate experiments 1 mgrm. Cu, 1 mgrm. Pb, and 1 mgrm. Hg were mixed with 1 mgrm. Cd; a distinctly yellow precipitate was obtained in each experiment.

About 50 mgrms. Cd as CdS were boiled for five minutes with 20 cc. of a mixture of one volume H_2SO_4 (1·20) and four volumes of water; the sulphide did not dissolve completely.

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.

(LONDON SECTION).

Ordinary Meeting, June 3rd, 1907.

Mr. R. J. FRISWELL in the Chair.

"*The Nature of the Changes Involved in the Production and Setting of Plaster-of-Paris.*" By W. A. DAVIS.

The contradictory character of the present knowledge of this problem is first discussed. Data are then adduced to show that the first change occurring in the dehydration of gypsum is the formation of a new orthorhombic form of the dehydrate, $CaSO_4,2H_2O$, which by loss of water subsequently gives the half hydrate, $CaSO_4,\frac{1}{2}H_2O$ (the essential constituent of ordinary plaster). The so-called "soluble anhydrite" is produced from gypsum, not directly as supposed by van't Hoff, but as a product of the further dehydration of the half hydrate. The conditions under which this change occurs and the manner in which it may be reversed are dealt with in detail. In the setting of plaster, gypsum is not immediately regenerated, but the second form of the dehydrate referred to above is first produced; it undergoes change into gypsum subsequently. Many of van't Hoff's conclusions concerning the changes occurring in the dehydration of gypsum are shown to be invalidated by incorrect assumptions; the problem being much more complicated than hitherto supposed.

"*The Influence of Temperature of Dyeing on Resolution.*" By W. B. DRAPER and A. WILSON.

Basic colours are absorbed by silk fibre in two ways. Above 40° a more permanent absorption of part of the dye takes place, which increases up to 100°. A similar effect is noticed with acid dyes on silk. Preliminary boiling with water or acid does not influence subsequent dyeing at low temperatures. A similar result is obtained with direct colours on cotton, so the reaction is a general one. The effect is absent when dyeing in alcohol. Fastness against light does not follow the temperature in same way.

"*Analysis of White Lead.*" By W. A. DAVIS and C. A. KLEIN.

The authors have investigated the sources of error in the different methods used in the analysis of white lead. These errors are much smaller in the case of dry white lead than in that of white lead ground in oil. In the latter case it is impossible to extract the oil completely, a small quantity (0·3 per cent) always remaining undissolved. This residual "oil" causes the results for CO_2 and H_2O obtained by the combustion method to be high—in the case of CO_2 an error of nearly 1 per cent may be so caused. Another and even more important source of error is the fact that white lead in contact with oil gradually undergoes a change in composition, so that analyses obtained with the same sample at different times give different results. Details are given of two methods for the accurate estimation of CO_2 in *dry* white lead, and also of a method for directly determining combined water.

"*The Loss of Nitre in the Chamber Process.*" (Part III.). By J. K. H. INGLIS.

The author, in continuation of earlier papers, has again analysed samples of the exit gases from sulphuric acid chambers by means of fractional distillation at low temperatures. Indirect analyses were almost completely avoided, and the results show the presence of small quantities of nitrous oxide and of appreciable quantities of higher oxides, the quantity of nitric oxide being considerable when the sulphur escape is high. There is still a considerable quantity of nitre unaccounted for, its loss being either due to reduction to nitrogen or to the whole of the nitric acid not being collected in this method of analysis.

"*Calorimeter for Volatile Liquid Fuels, Specially adapted for Petrol.*" By W. HANSEN RAWLES.

A development of the Darling calorimeter.

The liquid is burnt in a small brass lamp having asbestos wick and cap.

The combustion chamber stopper carries an electrical conductor for igniting the liquid and a rod to remove the lamp cap.

During the combustion the lamp is surrounded by cold water, which is finally driven by oxygen pressure into the outer vessel.

The gases bubble out from the base of apparatus into the outer water, run up a copper arch-sectioned spiral (round the combustion chamber), and escape into the air. Efficient absorption of heat is ensured.

This calorimeter, which was made for the author by A. Gallenkamp and Co., is applicable to solid and liquid fuels.

FARADAY SOCIETY.

Ordinary Meeting, May 28th, 1907.

Prof. A. K. HUNTINGTON in the Chair.

A PAPER entitled "*Contributions to the Chemistry of Gold,*" by Mr. F. H. CAMPBELL, M.Sc., was read in abstract by Mr. N. T. M. WILSMORE, M.Sc. (Will be inserted in full).

Dr. F. MOLLWO PERKIN read a paper on "*Reduction of some Oxides and Sulphides by means of Metallic Calcium.*"

The author first referred to the well-known powerful reducing action of aluminium, as, for example, its use in the preparation of chromium, ferrosilicon, and other metals and alloys, and its use in the form of "thermite" for welding purposes. He finds that metallic calcium is a still more powerful reducing agent than aluminium. For example, when molecular proportions of aluminium and ferric oxide are mixed together and ignited by means of a fuse of aluminium and barium peroxide, intense reaction ensues, and continues until all the oxygen has been removed from the ferric oxide, and aluminium oxide and metallic iron produced in its stead. When metallic calcium in the form of fine turnings is mixed with ferric oxide and ignited in a similar manner, the reaction is so intense that

the mixture is in large part ejected from the crucible. The reaction can be brought under control by mixing 30 to 40 per cent of calcium fluoride or 10 to 20 per cent of calcium oxide with the contents of the crucible. Boron can be obtained by igniting a mixture of boron trioxide with the calculated quantity of calcium and 5 to 10 per cent of calcium oxide. If no calcium oxide is added the reaction is too violent. It is, however, very difficult entirely to free the boron from calcium even after standing over hydrochloric acid for weeks; the boron invariably contains considerable quantities of calcium, which is probably present as calcium boride. When borax is carefully dried and mixed with calcium, and the mixture ignited by a fuse, the reaction completes itself without undue violence. On treating the reaction mixture with hydrochloric acid, brown amorphous boron is obtained in almost theoretical quantities; the product, however, always contains calcium, but can be used for preparing boron chloride and similar compounds. Rather anomalous results were obtained when sand (silicon dioxide) was ignited with calcium. Unless considerably less than the theoretical amount of calcium was used, not silicon but probably calcium silicide was obtained, because when the reaction mixture is placed in hydrochloric acid, large quantities of a spontaneously inflammable gas are given off; this gas is probably silicon hydride. The product remaining behind is silicic acid and calcium chloride. The results were the same when a mixture of aluminium and calcium was employed.

Attention was also drawn to the difficulty experienced in causing silica in the form of fine sand to react with metallic aluminium which was in the form of a rough powder. A similar difficulty was met with in the case of boric anhydride and aluminium. Galena does not yield metallic lead and calcium sulphide, but a greyish mass which gives off sulphuretted hydrogen when acted upon with acids, lead in the form of a salt being left in solution. Red phosphorus and calcium unite with explosive violence. Sulphur and calcium also react with great vigour. Manganese dioxide and calcium require to be mixed with 30 to 40 per cent of calcium fluoride, when a regulus of manganese can be obtained, otherwise the reaction is too violent. This is also the case with chromium oxide. When the experiments were first tried it was found that the reaction mixture always stuck to the crucible, and it was invariably necessary to break the crucible in order to obtain the product. Subsequently the difficulty was got over by lining the crucible with a paste made from slake lime and a strong solution of sodium silicate (water-glass); in the case of boron the solution used was generally borax. The crucible and lining were thoroughly dried, and were then ready for use. With crucibles so prepared there was never any difficulty in getting out the reaction product in the form of a lump without breaking the crucible.

Mr. F. E. Weston said that he had succeeded in reducing silica in the form of kieselguhr by means of aluminium. He had recently used aluminium in the reduction of titanium compounds.

Mr. W. P. Digby asked whether calcium would, like aluminium, prevent segregation in steel castings.

Prof. A. K. Huntington said that the state of division of the materials in these experiments was of paramount importance. He believed, answering Mr. Digby, that calcium had not proved a successful substitute for aluminium in pouring steel; the calcium oxide seemed to remain in the metal.

Prior to the Ordinary Meeting the Annual General Meeting of the Society was held, at which the Report of the Council and the Balance Sheet were duly approved, and the following Officers and Council elected for the Session 1907-8:—

President—Sir William Perkin, F.R.S.

Vice Presidents—G. T. Beilby, F.R.S.; R. A. Hadfield; Prof. W. Hittorf; Sir William Huggins, O.M., F.R.S.; Prof. A. K. Huntington; Prof. A. Schuster, F.R.S.; Prof. J. J. Thomson, F.R.S.

Treasurer—F. Mollwo Perkin, Ph.D.

Council—A. C. Claudet; S. Z. de Ferranti; F. W. Harbord; R. S. Hutton; T. M. Lowry; W. Murray Morrison; J. Swinburne, F.R.S.; N. T. M. Wilsmore; Prof. E. Wilson; J. L. F. Vogel.

NOTICES OF BOOKS.

Lubrication and Lubricants. By Leonard Archbutt, F.I.C., F.C.S., and R. Mountford Deeley, M.I.Mech.E., F.G.S. Second Edition. London: Charles Griffin and Co., Ltd. 1907.

The second edition of this treatise on the theory and practice of lubrication, and on the nature, properties, and testing of lubricants, contains some important fresh matter, both theoretical and practical. The authors have done much valuable pioneer work, and have, moreover, had opportunities of testing different lubricants and appliances for lubrication, and to their own knowledge, which they put at the disposal of their readers, they have added an exhaustive compilation of the researches of others, with the result that the work is of an extremely comprehensive nature. The first edition was at once accepted as practically invaluable to the engineer, and the second fully maintains its high reputation, every endeavour having been made to bring it up-to-date in all respects. The pages on the sources, preparation, and chief properties of mineral oils have been revised by Sir Boverton Redwood, and other experts have assisted the authors with advice and information relating to various oils suitable for the lubrication of different types of machines and engines.

Glues and Gelatine. By R. Livingston Fernbach. London: Archibald Constable and Co., Ltd. 1907.

The author of this book has done a service to manufacturers interested in the use of glue in calling their attention to the frauds which can be, and are, practised upon them, if they are content to entrust their interests into the hands of the glue maker, without attempting to test the value of the material supplied to them. The book contains details regarding the testing of glues for special purposes by chemical and mechanical means, and with its help the consumer should be able to acquire some idea whether he is getting full value for his money. The analytical operations are described sufficiently fully to enable a manager or foreman to understand something of the methods and results of analysis, although not to qualify as an analyst. The manufacture of glue is not discussed, the author being of the opinion that for the present old rule-of-thumb methods cannot be altogether supplanted by scientific procedure; however, when consumers have clearer ideas as to the standards they are entitled to expect the article delivered to them to come up to, an advance towards the adoption of more scientific methods will have been definitely made, and the author's aim is to collect data and suggest methods upon which these ideas can be based.

Van Nostrand's Chemical Annual, 1907. Edited by John C. Olsen, A.M., Ph.D. London: Archibald Constable and Co., Ltd. 1907.

This handbook contains much valuable information, and will be found a boon to busy men. It is conveniently arranged, and contains all the tables required for ordinary analytical work, together with full reference tables of the physical constants of the most important inorganic and organic compounds, besides specific gravity tables of various solutions, and also useful thermo-chemical data. In addition an attempt has been made to compile a list of the more important articles on chemical subjects which were published between January 1st, 1905, and June 1st,

1906, and this list, which contains more than a thousand references to chemical literature, will undoubtedly be much appreciated. The compilers have exercised an excellent discretion in their work, which will give great assistance to all who wish to keep their knowledge abreast with the times. In addition, a list of important books, published during the same period, is given with the published price, and, in the case of German books, references are frequently given to the number in the *Zeitschrift für Anorganische Chemie* in which reviews may be found. In view of the endeavours which have evidently been made by the compilers to ensure accuracy in other parts of the book, it is surprising to find that these book lists have been carelessly printed. Two misprints in well-known names on the first page raise suspicions as to the correctness of later parts, suspicions which further examination will show are not unjustified. However, this is a simple matter to remedy, and the new annual, it is to be hoped, has a long and useful life before it, for it fills a place at present unoccupied by any book in the English tongue.

Physikalisch-chemische Ubungen. ("Practical Physical Chemistry"). By Dr. W. A. Roth. Hamburg and Leipzig: Leopold Voss. 1907.

The needs of the beginner in the study of physical chemistry have been somewhat overlooked, because, rightly or wrongly, it is regarded frequently as a branch of chemistry which cannot profitably be taken up at an early stage in the student's career, although it has peculiar attractions for the research student, owing to the wide fields of investigation which are waiting for workers. However, this view is perhaps less widely held now than it was a short time ago, and books of elementary practical physical chemistry are beginning to make their appearance, such as the one under review, which is on the whole a satisfactory specimen of its kind. The experimental directions appear to be clear and easily understood, and thermo-chemistry is well treated; throughout the book the connections between the practical results obtained and the theoretical deductions from them are very clearly put before the worker, who is thus prevented as far as possible from degenerating into a follower of directions given in the form of recipes—a tendency in the young student which the elementary practical book has above all to combat. On the other hand, it cannot be said that the book is free from defects, some of which are not of a trivial nature. Among omissions may be specially regretted that of methods of determining viscosity and surface tension, while electro-chemistry is treated rather scantily. In describing the determination of vapour density by Victor Meyer's method the old form of apparatus is recommended instead of the new, which is a great improvement upon it, and is now almost universally adopted.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 21, May 27, 1907.

Double Sulphites of Hypovanadic Acid.—Gustave Gain.—The alkaline bases combine easily with hypovanadic acid in presence of sulphurous acid, giving well-defined double sulphites. These are obtained by treating ammonium metavanadate with a saturated solution of sulphurous acid, adding a solution of alkaline bisulphite, and evaporating slowly. In some cases it is necessary to evaporate *in vacuo*. The formulæ of the crystalline compounds prepared thus by the author are—

$3(SO_2V_2O_4)(SO_2K_2O).5H_2O$,
$3(SO_2V_2O_4)SO_2(NH_4)_2O.4H_2O$,
$(SO_2V_2O_4)2(SO_2Rb_2O).2H_2O$,
$(SO_2V_2O_4)3(SO_2Cs_2O).8H_2O$,
$3(SO_2V_2O_4)(SO_2Tl_2O).8H_2O$,
$5(SO_2.V_2O_4)(SO_2Na_2O).2H_2O$,
$(SO_2V_2O_4)5(SO_2Li_2O).8H_2O$.

Selenide of Lead.—H. Pélabon.—Lead combines directly with selenium, and the compound thus obtained forms homogeneous mixtures with excess of metal or metalloid. The author has constructed fusibility curves of these mixtures, taking as abscissæ the values R of the ratio of the mass of the selenium to the total mass, and as ordinates the corresponding values of the temperature of solidification of the previously fused mixtures. If R exceeds 5 and continues to increase, the temperature of solidification of the corresponding mixtures increases regularly till it attains its maximum 1065° when R is about 27. This temperature is the melting-point of lead selenide, PbSe, in which R = 27·62. When the amount of selenium varies from 0 to 27 per cent, the liquid obtained by fusing the two substances is a homogeneous mixture of lead selenide, PbSe, and metallic lead. Mixtures which contain more than one atom of selenium to one atom of lead readily lose selenium when heated. For all mixtures in which the amount of selenium present lies between 27 and 45 per cent the temperature of solidification is in the neighbourhood of 673°. When the selenium exceeds 45 per cent the liquid separates into two layers. The denser solidifies at 673°, giving a grey-black solid, while the upper layer is pure selenium with a much lower melting-point. Between 300° and 600° the liquids can readily be separated by decantation, and the selenium thus obtained contains no trace of lead. The analysis of the liquid which solidifies at 673° shows that it is not the compound $PbSe_2$, there being always a slight excess of selenium. It appears to be a saturated solution of selenium in the selenide PbSe, and when it is allowed to solidify *in vacuo* vapours of selenium escape rapidly from the mass.

Methyl Ethers of Allyl and Propargyl Carbinol.—M. Lespieau.—If allyl bromide and chloromethyl ether are added to magnesium in the proportion of 60 grms. of brominated compound, and 40 grms. of chloromethyl ether to 12 grms. of magnesium, the metal will dissolve totally if the whole is well stirred. If then water is added and the liquid distilled, ordinary ether, biallyl, and the compound $CH_2=CH—CH_2—CH_2OCH_3$ are formed. It is almost impossible to separate the last by fractional distillation, but if bromine is first added and the liquid is then distilled the ether $CH_2Br—CHBr—CH_2—CH_2OCH_3$, which boils at 90° under 13 mm., can readily be separated from the tetrabromide of biallyl, which passes over at 180° under the same pressure. The ether $CH_2Br—CHBr—CH_2—CH_2OCH_3$ reacts with sodium ethylate, giving almost equal quantities of the two unsaturated brominated ethers, $CH_2=CBr—CH_2—CH_2OCH_3$ and $CHBr=CH—CH_2—CH_2OCH_3$, both of which when treated with ordinary or alcoholic potash give the true acetylenic compound $CH\equiv C—CH_2—CH_2OCH_3$.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 8, 1907.

Diphenylurea Chloride as a Reagent for Phenols.—J. Herzog.—Diphenylurea chloride is an excellent reagent for phenols, with which it forms crystalline compounds. Tertiary alcohols in general do not give this reaction. The behaviour of diphenylurea chloride shows a characteristic difference with the hydroxyl groups of alcohols and those of phenols. Of all the phenols and their derivatives which the author has investigated, the only ones which give no crystalline urethanes are the phenol-carbonic acids. In order to prepare and purify the different phenol-urethanes

the phenol is heated in a flask in boiling water for an hour with four times its weight of pyridine and the molecular weight of diphenylurea chloride; then the solution is stirred with water, when a red crystalline mass is obtained. When the water has been poured off and the crystals have been dried superficially, they are re-crystallised from ligroin or alcohol. The reaction is as follows:—The diphenylurea chloride first forms an addition product with pyridine, which in presence of phenols gives pyridine hydrochloride and phenol urethane:—

$$C_5H_5N<\begin{matrix}Cl\\CO.N<\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\end{matrix}+R.OH=$$

$$=C_5H_5{:}\,N<\begin{matrix}Cl\\H\end{matrix}+RO.CO.N<\begin{matrix}C_6H_5\\C_6H_5\end{matrix}$$

The diphenyl urethanes can very easily be saponified by heating to 100° for two hours with alcoholic potash. They can conveniently be employed for the identification of the phenols, and as the yield of them is very good a weight of 0·1 grm. of phenol is sufficient for its identification by this method.

New Colour Reaction of Ligno-cellulose.—Alvin S. Wheeler.—The salts of nitroaniline give a characteristic blood-red coloration with ligno-cellulose. An aqueous solution of the hydrochloride of nitroaniline (preferably the para-compound) produces first a yellow coloration with materials containing ligno-cellulose, and this yellow colour changes to deep red in a few hours. The best results are obtained in presence of free acid, and if 2 grms. of paranitroaniline are dissolved in 100 cc. of hydrochloric acid of specified gravity 1·06, and this solution is used hot, if ligno-cellulose is present an immediate blood-red coloration is obtained.

2 : 1-Ferro-ferric Oxide.—Otto Hauser.—When ferro-ferric ammonium carbonate, $Fe^{II}(NH_4).(CO_3)_3Fe^{III}O,H_2O$, prepared by the method described by the author (*Berichte*, 1905, xxxviii., 2707) is shaken up with hot strong caustic potash, through which a current of coal-gas is passing, a black oxide separates, which can readily be filtered off and washed. This black oxide is not attracted by a magnet and is characterised by its extreme instability in air, which properties distinguish it from the oxides described by Haber and Lefort. Determinations of the iron present as oxide and also the total iron were made, the mean result being 2·97 : 1 of total iron to oxide iron. Thus the existence of the oxide $Fe_6O_7=4FeO.Fe_2O_3$ is proved. The composition of the hydrate dried at 100° is $Fe_6O_7.5H_2O$. The sesquioxide hydrate, which is produced when the above compound is exposed to the air, differs from it in colour, being very much darker. Moreover, it is strongly magnetic. Its formula is $Fe_2O_3.H_2O$. When heated to about 300° it yields the anhydride. The specific gravity of the magnetic sesquioxide hydrate is 3·58, that of the magnetic sesquioxide dried at 300° is 4·35, while when it is heated to a still higher temperature it loses its magnetism and has the specific gravity 5·15. The oxide Fe_6O_7 is the base of the mineral lievrite, which has the composition $(SiO_4)_2(Fe^{III}.OH)(Fe_2^{II}Ca)$, similar to $(CO_3)_3.Fe^{III}O.Fe_2^{II}(NH_4)H_2O$.

Complex Compounds of Organic Imides.—L. Tschugaeff.—If alkali hydroxides are allowed to act upon copper salts (preferably the acetate) and excess of succinimide in aqueous alcoholic solution, a series of characteristic complex substances is obtained, the composition of which may be expressed by the general formula $Cu(Sn)_4Me_2.nH_2O$ or $(Sn)_2Cu.2SnMe.nH_2O$, where Me stands for a metal of the alkali group. The potassium compound is light reddish violet, the rubidium and cæsium compounds are both reddish violet, the sodium compound is blue, and the lithium compound ultramarine blue. In the solid state the compounds are stable; when water is added to them they undergo hydrolysis, and copper hydroxide or basic copper salt separate. In presence of dilute alcohol containing alkali and excess of succinimide the solutions of the complexes are stable. Dilute acids effect the following decomposition of the potassium complex quantitatively: — $K_2CuSn_4+4HA=4SnH+2KA+CuA_2$. The corresponding nickel compounds can be prepared exactly similarly. They are yellow crystalline substances and are decomposed by water more readily than the copper derivatives. These copper and nickel succinimide complexes recall the copper and nickel compounds of biuret. The reddish violet colour of the complex anion $CuSn_4$ seems to be characteristic of the potassium, rubidium, and cæsium compounds, and the blue sodium and lithium compounds cannot belong to the same series. It is noteworthy that the number of molecules of water of crystallisation is even in the case of the potassium, rubidium, and cæsium compounds (6, 2, and 2 respectively), and odd in the case of the sodium and lithium compounds (5 and 1 respectively.)

Compounds of Pentavalent Chromium. (III.).—R. F. Weinland and Max Fiederer.—When glacial acetic acid is saturated with hydrochloric acid, chromic acid is dissolved in it and allowed to stand for some time, and then pyridine (dissolved in hydrochloric and acetic acids) is added, a salt separates out in reddish brown flakes. This salt has the formula $CrOCl_3.C_5H_5N.HCl$, and is identical with the salt the authors obtained from aqueous hydrochloric acid. The quinoline salt, $CrOCl_3.C_9H_7N.HCl$, obtained from an aqueous solution contains two molecules of water of crystallisation, while when prepared by the glacial acetic acid method it contains no water. The alkali salts of the type $CrOCl_3.2KCl$ can also be prepared more conveniently by the glacial acetic acid than by the aqueous method.

Complex Compounds of Pentavalent Vanadium with Tetravalent Elements.—Wilhelm Prandtl.—When stannic chloride solution is added to sodium orthovanadate solution, and the mixture is neutralised, an amorphous yellow precipitate separates. It is soluble in alkalis and acids and is decomposed by water. When a large excess of vanadium is present during the precipitation it has the formula $3SnO_2.V_2O_5.Na_2O.xH_2O$ or $4SnO_2.V_2O_5.Na_2O.xH_2O$. When this yellow stannic vanadate is dissolved in hot concentrated caustic soda white crystalline needles separate. These are compounds of sodium stannate and sodium orthovanadate, or sodium stannate-vanadates, containing large quantities of water of crystallisation. They are of varying composition, and according to the proportions of the reagents and the temperature and concentration of the solutions, crystals containing more or less tin are obtained, their formulæ being $Na_2SnO_3.3Na_3VO_4.32H_2O$, $Na_2SnO_3.4Na_3VO_4.48H_2O$, $Na_2SnO_3.5Na_3VO_4.64H_2O$, $Na_2SnO_3.6Na_3VO_4.80H_2O$, The tendency of sodium stannate vanadates to form supersaturated solutions is very marked. When their dilute solutions are evaporated, they yield hard, transparent, prismatic crystals of any desired size. Concentrated solutions often do not crystallise for days, but the addition of a small crystal causes them to solidify at once. They take up carbon dioxide in air, and when kept in a desiccator over sulphuric acid, the crystals crumble to a white powder and lose all their water of crystallisation. Analogous potassium or ammonium stannate-vanadates could not be prepared, but when sodium stannate and sodium phosphate or arsenate in alkaline solution were mixed, or when stannic phosphate or arsenate was dissolved in caustic soda, white crystalline salts of the following composition were obtained: —$Na_2SnO_3.4Na_3PO_4.48H_2O$, $Na_2SnO_3.5Na_3PO_4.60H_2O$, $Na_2SnO_3.6Na_3PO_4.72H_2O$, $Na_2SnO_3.4Na_3(P,V)O_4.48H_2O$, $Na_2SnO_3.5Na_3AsO_4.60H_2O$. The two minerals — dahllite, $CO_2.3P_2O_5.9CaO.\frac{1}{2}H_2O$, and staffelite, $CO_2.3P_2O_5.9CaO.CaF_2.H_2O$—are analogous to these compounds of sodium stannate with sodium orthovanadate, phosphate, and arsenate. If the fluorine of staffelite is replaced by the equivalent quantity of oxygen, their formulæ may be written $CaCO_3.2Ca_3(PO_4)_2.\frac{1}{2}H_2O$ (dahllite) and $CaCO_3.3Ca_3(PO_4)_2.H_2O$ (staffelite). The difference between the two compounds is one molecule of calcium orthophosphate $Ca_3(PO_4)_2.\frac{1}{2}H_2O$.

Anhydrous Thiocyanic Acid.—Arthur Rosenheim and Richard Levy.—Klason's method of preparing anhydrous thiocyanic acid by leading the vapour of a ten per cent aqueous acid solution over calcium chloride warmed to 40° and then cooling strongly, leads to the formation of a mixture of condensed sulphuretted hydrogen, sulphur dioxide, carbon disulphide, and hydrogen cyanide, containing 40 or 50 per cent of thiocyanic acid. If, however, dehydrated powdered potassium thiocyanide is mixed with its own weight of phosphorus pentoxide in a distilling flask, and the delivery tube is connected with a small gas washing flask which can be cooled in a Dewar's vessel, and the whole is well cooled, the whole apparatus being filled with hydrogen, upon allowing sulphuric acid to drop into the flask colourless fumes are evolved which condense to a white crystalline mass. The vapours in the distilling tube gradually turn yellow and then red, and the contents of the flask also turn yellow, owing to the formation of decomposition products of thiocyanic acid. The analysis of the white crystalline mass shows that it consists only of thiocyanic acid. It can be kept for hours in a closed tube at 0°. Above this temperature it quickly fuses, turning yellow, the melting-point being about 5°. The acid has an irritating smell, and it has strong corrosive action on the skin.

MEETINGS FOR THE WEEK.

TUESDAY, 25th.—Faraday Society, 8. "Thermo-chemistry of Electrolysis in Relation to the Hydrate Theory of Ionisation," by W. R. Bousfield and T. M. Lowry. "Influence of Non-electrolytes and Electrolytes in the Solubility of Gases in Water—The Question of Hydrates in Solution," by J. C. Philip. "Dissociation of Hydrates as indicated by their Equilibrium Curves," by A. Findlay. "Hydrates in Solution—Discussion of Methods proposed for Determining Degree of Hydration," by G. Senter. General Discussion on Hydrates in Solution.

FRIDAY, 28th.—Physical, 5. (At the City and Guilds' Central Technical College, Exhibition Road). J. T. Irwin—Demonstration of the uses of his Hot-wire Oscillographs and Hot-wire Wattmeters. J. S. Dow—(1) A Cosine Flicker Photometer; (2) Some Phenomena in Colour Vision. W. E. Ayrton and T. Mather—(1) Description and Exhibition of Student's Apparatus for Measuring Permeability and Hysteresis; (2) Design of Chokers.

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THE CHEMICAL NEWS.

Vol. XCV., No. 2483.

ON THE CALCULATION OF PHYSICO-CHEMICAL CONSTANTS.

By H. STANLEY REDGROVE, F.C.S.

Thermo-chemical Constants of the Hydrocarbons.

The heat of combustion of a hydrocarbon is derived from several sources. Consider the case of the general hydrocarbon,—

$$nC + 2(n + 1 - a - 2b - f)H + (n + f - a - b - 1)L_1 + aL_2 + bL_3$$

The heat of combustion of one molecule of this hydrocarbon is the algebraic sum of the following heats :—

1. The heat due to the severance of $2(n + 1 - a - 2b - f)$ C . H links.
2. The heat due to the severance of $\frac{1}{2}(n + 1 - a - 2b - f)$ O : O links.
3. The heat of formation of $(n + 1 - a - 2b - f)$ molecules of water from H and O atoms.
4. The heat due to the severance of $(n + f - a - b - 1)$ C . C links.
5. The heat due to the severance of a C : C links.
6. The heat due to the severance of b C : C links.
7. The heat due to the severance of n O : O links.
8. The heat of formation of n molecules CO_2 from C and O atoms.

The coefficients of the Heats 1, 2, and 3 are always in the ratio $2 : \frac{1}{2} : 1$; therefore their algebraic sum can be considered as one constant ; likewise the algebraic sum of Heats 7 and 8 may be considered as one constant.

Dealing with grm.-molecular weights, and using the notation already adopted :—Σ Heats 1, 2, and 3 = $2(n + 1 - a - 2b - f)$ H cals. Heat 4 = $(n + f - a - b - 1)L_1$ cals. Heat 5 = aL_2 cals. Heat 6 = $6L_3$ cals. Σ Heats 7, 8 = nC cals.

The author has already shown that the values of these constants are unknown ; the values of the "fundamental constants" $\alpha(=C + 4H)$, $\beta(=2H - L_1)$, $\gamma(=4H - L_2)$, and $\delta(=6H - L_3)$ (Chemical News, vol. xcv., p. 193, see Note) can, however, be easily calculated thus :—

The value of $\alpha = C + 4H$ (methane) can be found experimentally.

The difference between the molecular heats of combustion of two adjacent homologues gives $C + 2H + L_1$, thus :—

Ethane—methane = (369·0 − 210·8) cals. = 158·2 cals.
Propane—ethane = (527·5 − 369·0) cals. = 158·5 cals., &c.
$C + 4H - (C + 2H + L_1) = 2H - L_1 = \beta$.

(Note.—In order to perfectly justify this statement with regard to thermo-chemistry, it is necessary to point out wherein Thomsen's system fails. No long discussion will be attempted, as several criticisms from other authors have already appeared. Thomsen's calculations appear to contain two assumptions, which are not justified :—1. That CO has the formula C=O ; *à priori* C≡O is equally as likely ; and, moreover, what little evidence we have appears to be in favour of this latter alternative. 2. That the heat of formation of one molecule CO from one atom C and one atom O, equals the heat of formation of one molecule CO_2 from one molecule CO and one atom O. Thomsen has himself shown (according to his system) that the thermal value of O varies according to the groups with which it is combined, rendering the above assumption inadmissable).

TABLE I.—Hydrocarbons.

1. Hydrocarbon.	2. Formula.	3.	4. M.H.C., constant volume (Thomsen).	5. M.H.C. calculated.	6. Diff. between cols. 4 and 5.	7. Percentage error.	8. Valency number (W).	9. (M.H.C) ÷ W.	10. W × 26·25.	11. Diff. between cols. 4 and 10.
			Cals.	Cals.	Cals.			Cals.	Cals.	Cals.
Methane	C + 4H	α	210·8	210·8	0·0	0·00	8	26·4	210·0	+ 0·8
Ethane	2C + 6H + L_1	2α − β	369·0	369·1	+ 0·1	+ 0·03	14	26·3	367·5	1·5
Propane	3C + 8H + 2L_1	3α − 2β	527·5	527·4	− 0·1	− 0·02	20	26·4	525·0	2·5
Trimethylmethane	4C + 10H + 3L_1	4α − 3β	685·2	685·7	+ 0·5	+ 0·07	26	26·4	682·5	2·7
Tetramethylmethane	5C + 12H + 4L_1	5α − 4β	844·8	844·0	− 0·8	− 0·09	32	26·4	840·0	4·8
Di-isopropyl	6C + 14H + 5L_1	6α − 5β	1002·3	997·2	+ 5·1	+ 0·51	38	26·2	997·5	+ 0·3
Ethylene	2C + 4H + L_2	2α − γ	332·2	332·6	+ 0·4	+ 0·12	12	27·7	315·0	− 17·2
Propylene	3C + 6H + L_1 + L_2	3α − β − γ	490·3	490·9	− 0·4	− 0·08	18	27·3	472·5	18·8
Trimethylene	3C + 6H + 3L_1	3α − 3β	474·9	498·0	− 23·1	− 4·64	18	27·7	472·5	25·5
iso-Butylene	4C + 8H + 2L_1 + L_2	4α − 2β − γ	648·9	649·2	+ 0·3	+ 0·05	24	27·0	630·0	18·9
iso-Amylene	5C + 10H + 3L_1 + L_2	5α − 3β − γ	806·2	807·5	+ 1·3	+ 0·16	30	26·9	787·5	18·7
Diallyl	6C + 10H + 3L_1 + 2L_2	6α − 3β − 2γ	930·8	929·3	− 1·5	− 0·16	34	27·4	892·5	37·3
Acetylene	2C + 2H + L_3	2α − δ	309·2	308·6	− 0·6	− 0·19	10	30·9	262·5	46·7
Allylene	3C + 4H + L_1 + L_3	3α − β − δ	466·4	466·9	+ 0·5	+ 0·11	16	29·2	420·0	46·4
Dipropargyl	6C + 6H + 3L_1 + 2L_3	6α − 3β − 2δ	881·4	881·3	− 0·1	− 0·01	30	29·4	787·5	93·9
Benzene	6C + 6H + 3L_1 + 3L_2	6α − 3β − 3γ	797·9	840·3	+ 42·4	− 5·6	30	26·6	787·5	10·4
	6C + 6H + 9L_1	6α − 9β		792·3	− 5·6					
Toluene	7C + 8H + 4L_1 + 3L_2	7α − 4β − 3γ	953·9	998·6	+ 44·7	+ 4·7	36	26·5	945·0	8·9
	7C + 8H + 10L_1	7α − 10β		950·6	− 3·3					
Mesitylene	9C + 12H + 6L_1 + 3L_2	9α − 6β − 3γ	1280·0	1315·2	+ 35·2	+ 2·8	48	26·7	1260·0	20·0
	9C + 12H + 12L_1	9α − 12β		1267·2	− 12·8					
Pseudocumene	9C + 12H + 6L_1 + 3L_2	9α − 6β − 3γ	1279·2	1315·2	+ 36·0	+ 2·8	48	26·7	1260·0	19·2
	9C + 12H + 12L_1	9α − 12β		1267·2	− 12·0					

† Ladenburg's or Claus's formula: (without adding the value due to tension).

* Kekulé's formula.

The difference between the molecular heats of combustion of a saturated hydrocarbon, $nC+(2n+2)H+(n-1)L_1$, and the two corresponding unsaturated hydrocarbons, $nC+2nH+(n-2)L_1+L_2$ and $nC+(2n-2)H+(n-2)L_1+L_3$, gives $2H+L_1-L_2$ and $4H+L_1-L_3$.

$$(2H+L_1-L_2)+(2H-L_1) = 4H-L_2 = \gamma.$$
$$(4H+L_1-L_3)+(2H-L_1) = 6H-L_3 = \delta.$$

Or the values of the various hydrocarbons may be equated to the hydrocarbons (for which they are respectively obtained) in terms of the fundamental constants, and the equations solved in any convenient manner.

In order to obtain correct results, if the molecular heats of combustion have been found experimentally for constant pressure, a correction must be applied for constant volume.

In Table I. will be found the molecular heats of combustion of several hydrocarbons found by Thomsen ("Thermo-chemical Researches," 1906, German Edition); those not already corrected by him have been corrected by the author.

The values of the "fundamental constants" calculated from these results are:—α = 210·8 cals., β = 52·5 cals., γ = 89·0 cals., δ = 113·0 cals.

(The values already published were calculated for uncorrected molecular heats of combustion, and are therefore slightly higher than the above. They are sufficiently accurate for approximate calculations).

The molecular heats of combustion of the hydrocarbons have been calculated from these values, with the following interesting results (see Table I.).

Out of fifteen aliphatic hydrocarbons, the error in the case of thirteen is below 0·2 per cent, proving the additive nature of molecular heats of combustion. The error in the case of di-isopropyl is only about 0·5 per cent, and is probably experimental. The very large difference between the experimental and calculated values for trimethylene cannot be thus explained; the question will be considered hereinafter.

In passing we may notice an interesting hypothesis lately proposed by Gervaise le Bas (*Proc. Chem. Soc.*, xxiii., 134) of which only a preliminary note has appeared.

This author states that the heats due to the dissociation of the atoms (*i.e.*, the severance of the linkages) are negligibly small compared to the heats due to the combination of the dissociated atoms with oxygen. As the values of these respective heats are unknown this statement is pure assumption, and is proved to be wrong by the fact that the differences between the various carbon links have considerably large values, showing that at least two out of the three forms of carbon links have considerably large values.

The hypothesis referred to is, the molecular heats of combustion of hydrocarbons are proportional to their valency numbers W; the author cites as an example that the molecular heat of combustion of a normal paraffin, C_nH_{2n+2}, in the gaseous state is given by the expression M.H.C. $(6n+2)c = Wc$; where c = heat equivalent of one hydrogen atom in large calories. He uses the value c = 26·46 (mean). The heat equivalent of a hydrogen atom is, however, unknown, but c approximately = $\frac{1}{4}\beta = H-\frac{1}{2}L_1$; making this alteration, the above expression is correct, but it does not hold for unsaturated hydrocarbons, and appears to be only a lengthy way of stating that $4\beta = \alpha$ (approximately).

One would naturally think that any laws relating to molecular heats of combustion would hold for true molecular heats of combustion, *i.e.*, at constant volume.

In Table I. is given (M.H.C.÷W) and Wc for the corrected values, in which case c = 26·25. The figures speak for themselves.

To return, however, to a consideration of trimethylene. If a C : C link were a double link in an arithmetical sense we should have $L_2-2L_1 = 0$, whereas actually $L_2-2L_1 = 2(2H-L_1)-(4H-L_2) = 2\beta-\gamma$ = 16·0 cals.; similarly, L_3-3L_1 = 44·5 cals. We know, however, from pure chemistry that a "double" link is not an arithmetical double link, but in so far as stablility is concerned less than a single link.

Thermo-chemistry is in agreement with this fact; for, as we should suppose, less energy is required to sever an unstable bond, or more energy is given out at its severance, than in the case of a stable bond.

The instability of C : C and C ⋮ C links find a mathematical interpretation in von Baeyer's tension theory. Accepting this theory we know that although a C : C link consists of two single links, it is also productive of a certain amount of tension, which renders it less stable than a single link; if we represent the thermal value of this tension by T_2, then $2L_1+T_2 = L_2$, whence T_2 = 16·0 cals. Similarly, if T_3 is the tension in a C ⋮ C link, then $3L_1+T_3 = L_3$, whence T_3 = 44·5 cals.

In trimethylene, although there are no C : C or C ⋮ C links, we know from Baeyer's tension theory that a certain amount of tension is produced in it, thus explaining the instability of the substance. Consequently, the molecular heat of combustion of trimethylene will be greater than $3C+6H+3L_1$ (= 474·9 cals.) by the thermal value of this tension, which is given by experiment as 23·1 cals.

Turning our attention to the aromatic hydrocarbons, we find, as we should expect, Kekulé's formula gives too high values. The formula $6C+6H+9L_1$ (Ladenburg's or Claus's), for benzene gives fairly good values apparently at first sight.

Applying, however, the knowledge gained relative to tension we are led to the conclusion that Ladenburg's formula would give very much higher values than those calculated on the supposition that benzene is $6C+6H+9L_1$, for a substance having Ladenburg's formula would contain two trimethylene rings and three tetramethylene rings; consequently, we must add to the values calculated as above the thermal value of the tension thus produced, which must be greater than 2(23·1) cals., *i.e.*, 46·2 cals. The true theoretical values would therefore be over 30 to 40 cals. too high.

Claus's formula also contains tetra-methylene rings, which would cause the theoretical values to be higher than calculated on the supposition that benzene is $6C+6H+9L_1$.

The thermo-chemistry of benzene is in agreement with the pure chemistry of the substance, showing, as it does, its saturated and stable nature. Comparing the molecular heats of combustion found experimentally with those calculated for the fully saturated formulæ, we are led to the conclusion that there is just a little tension in the molecules of aromatic hydrocarbons, less than that produced by one C : C link. Probably this has been best expressed up to the present time by Baeyer's centric formula, although this is not altogether satisfactory.

The Polytechnic, Regent Street, W.

Quantitative Determination of Hydroxyl Groups by means of Magnesium Organic Compounds.—Th. Zerewitinoff.—The author describes an apparatus in which magnesium-methyl iodide can be used to determine hydroxyl quantitatively. He recommends the use of pyridine as solvent and measures directly the volume of methane generated. This method can be applied not only to alcohols and phenols of simple constitution, but also to compounds of complicated structure, such as sugars, acids, oximes, &c. The method is quite accurate enough to leave no doubt about the number of hydroxyls present in the compound investigated. It is quickly carried out at the ordinary temperature, and is very simple, while the possibility of secondary reactions is practically excluded.—*Berichte*, xl., No. 8.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part II.—Analysis of the Silver, Copper, and Tin Groups.

By ARTHUR A. NOYES and WILLIAM C. BRAY.

(Concluded from p. 296).

Confirmatory Experiments and References (*contd.*).

Analysis of the Tin Group.

P. 41, N. 1 : *Detection of the Tin Group by the appearance of the* HCl *Precipitate from the Ammonium Polysulphide Solution.*—Separate 10 cc. portions of the ammonium polysulphide reagent (see P. 41, N. 2) were diluted to known volumes in some experiments with hot water, and in others with cold water ; the solutions were then made acid by adding HCl slowly, and the mixtures were shaken and allowed to stand ; from cold solutions of a total volume of 30 to 50 cc. the sulphur separated as a pure white, finely divided precipitate, which coagulated slowly on shaking, and had then only a faint yellow tinge which did not change on warming. From more concentrated solutions, and especially from hot solutions, the yellow colour after coagulation was more pronounced. Separate 10 cc. portions of the ammonium polysulphide reagent containing 1 mgm. As were diluted with 20 cc. and with 40 cc. water ; HCl was slowly added until the solutions were acid ; the mixtures were shaken and allowed to stand ; the precipitate had at first the appearance of pure sulphur, but it coagulated more quickly, became flocculent, and turned brilliant yellow. Further experiments showed that the coagulation and change of colour took place more quickly when the mixture was slightly warmed after coagulation.

The experiment was repeated, using 1 mgrm. Sb instead of As ; the HCl precipitate remained white as long as the solution remained alkaline, but on further addition of HCl the orange colour of the Sb_2S_5 became very apparent ; the precipitate quickly coagulated and became flocculent. The experiment was repeated with 1 mgrm. Sn : the HCl precipitate had a very faint yellow tinge ; it coagulated only slowly, and appeared like the pure sulphur precipitate, except that it had a much darker yellow colour. The experiment was repeated with 1 mgrm. Cu as $CuSO_4$; a dark orange-yellow (liver-coloured) precipitate was obtained. The experiment was repeated with 1 mgrm. Hg as $HgCl_2$; the HCl precipitate was nearly white, but when warmed slightly it became dark grey in colour.

Colour of a Mixture of Tin and Antimony Sulphides.—500 mgrms. Sn as $SnCl_2$ and 200 mgms. Sb as $SbCl_3$ were slowly added to 10 cc. of a warm ammonium polysulphide solution, and the clear solution obtained was at once acidified with HCl ; a brown precipitate separated, which slowly became dark grey in colour. The experiment was repeated, except that the ammonium polysulphide solution was cooled and diluted to about 40 cc. and HCl was slowly added ; the precipitate was at first yellow with an orange tint, but on standing it slowly became darker, assuming first a brown and finally a dark grey colour. These precipitates were treated by P. 42—47 ; the antimony and tin dissolved completely in HCl (1·20) (P. 42), and the antimony was completely precipitated in P. 45 as an orange precipitate.

P. 41, N. 2 : *Solubility of Tin-group Sulphides in* NH_4OH.—See C. E., P. 22, N. 1.

For evidence that salts of intermediate sulpho-oxyacids of arsenic are formed when As_2S_5 is dissolved in an alkali, see McCay (*Ber.*, 1899, xxxii., 2171 ; *Zeit. Anorg. Chem.*, 1901, xxv., 459) ; McLouchlan (*Ber.*, 1901, xxxiv., 2166) ; Weinland and Lehman (*Zeit. Anorg. Chem.*, 1901, xxvi., 322). Treadwell ("Qual Anal.", p. 188, 1902) concludes that K_3SbO_3 is not formed by the action of KOH on Sb_2S_3 according to the equation $Sb_2S_3 + 6KOH = K_3SbO_3 + K_3SbS_3 + 3H_2O$, because this solution is stable when diluted, while a solution of K_3SbO_3 is not.

For evidence that the precipitation of arsenic is incomplete when a solution of As_2S_5 in an alkali is made acid, see Weinland and Lehman, *loc. cit.*, and Vanino and Griebel, *Zeit. Anal. Chem.* 1901, xl., 589.

Presence of Copper and Mercury in the Tin Group.—For the solubility of CuS and HgS in NH_4OH and in ammonium mono- and polysulphide, see C. E., P. 22, N. 4. For the fact that copper and mercury will divide in the heating with HCl (1·20), see C. E., P. 42, N. 6. That the presence of even 2 mgrms. Cu or of Hg does not interfere with the detection of arsenic is shown in C. E., P. 43, N. 3. That the same amount of copper or mercury does not prevent the detection of antimony is shown in C. E., P. 46, N. 1.

P. 42, N. 1 : *Solubility of* Sb_2S_5 *in* HCl (1·20).—500 mgrms. Sb as sulphide, freshly precipitated from an ammonium polysulphide solution, and therefore consisting mainly of Sb_2S_5, were treated according to the procedure ; nearly all the antimony dissolved, but the sulphur residue had an orange-red colour. The residue was treated a second time in the same way, and the HCl solution diluted and saturated with H_2S ; a small precipitate of Sb_2S_5 estimated to contain 1 or 2 mgrms. Sb formed. The sulphur residue was again treated with HCl ; scarcely any Sb dissolved, although the residue still had a distinct orange colour.

A mixture of 1 mgrm. Sb as Sb_2S_5 with 500 mgrms. As as As_2S_5 (freshly precipitated from an ammonium polysulphide solution, and carefully dried by suction) was treated by the procedure, and the residue subjected to a second and then to a third treatment ; the separate HCl solutions were diluted and treated with H_2S by P. 45 ; the first solution contained about 0·6 mgrm. Sb, the second about half this amount, and the third only a trace. This experiment was repeated, except that the sulphides were not carefully dried before adding HCl (1·20) ; the second HCl solution contained more Sb than the first, thus showing that the presence of water interferes with the action of the HCl.

Formation of $SbCl_3$ *by Dissolving* Sb_2S_5 *in* HCl.—See Classen and Bauer (*Ber.*, 1883, xvi., 1067).

P. 42, N. 2 : *Solubility of* As_2S_5 *in* HCl (1·20).—Seven different 500 mgrm. portions of As as As_2S_5, freshly precipitated from an ammonium polysulphide solution, were treated by the procedure, and the filtrates were warmed and saturated completely with H_2S ; only a faint precipitate resulted, in no case corresponding to more than a small fraction of a mgrm. of arsenic. The experiment was repeated, except that the HCl (1·20) was boiled gently for five minutes ; the filtrate was found to contain 5 to 10 mgrms. As. The vapours given off blackened lead acetate paper held above the flask.

P. 42, N. 3 : *Solubility of* As_2S_3 *in* HCl (1·20).—Six separate 500 mgrm. portions of As as As_2S_3, freshly precipitated from H_3AsO_3 solution by H_2S in five of the experiments and by acidifying a solution of As_2S_3 in NH_4OH in the remaining one, were treated by the procedure, and the filtrate saturated with H_2S ; in each experiment distinct precipitates of As_2S_3 were obtained, which were estimated to contain between 1 and 5 mgrms. As. The experiments were repeated, except that a slow current of H_2S was passed through the HCl during the experiment ; the filtrates then gave with H_2S scarcely any precipitate. A solution of 100 mgrms. As as As_2O_3 in 20 cc. HCl (1·20) was saturated with H_2S for five minutes at about 90°, the solution decanted off, water added, and H_2S again passed in ; no more precipitate separated.

P. 42, N. 6 : *Solubility of* CuS *and* HgS *in* HCl.—Ten mgrms. Cu as CuS and 10 mgrms. Hg as HgS, freshly precipitated were treated in separate experiments by P. 42 ; the greater part, but not all, of each of the precipitates was dissolved.

**Solubility of* TeS_2 *in* HCl (1·20).—Fifty mgrms. Te as

* From the *Technology Quarterly*, xix., No. 3, September, 1906.

TeO_2 dissolved in HCl were added to 10 cc. ammonium polysulphide; the solution was treated by P. 41, the black HCl precipitate was heated with HCl (1·20) by P. 42, and the filtrate was saturated with H_2S; a precipitate formed estimated to contain about 1 to 2 mgrms. Te. The experiment was repeated, except that the HCl solution was kept saturated with H_2S; in this case no tellurium dissolved.

**Insolubility of Sulphides of* Pt, Au, Se, *and* Mo *in* HCl (1·20).—Twenty mgrms. Pt, 10 mgrms. Au, 50 mgrms. Se, and 50 mgrms. Mo, all as sulphides precipitated by acidifying an ammonium polysulphide solution, were in separate experiments digested at about 90° for ten minutes with 10 cc. HCl (1·20), diluted, and filtered, as described in P. 42; the filtrates were saturated with H_2S at 100°, diluted to 50 cc., again heated, and saturated with H_2S; no precipitate separated in any case, not even after several minutes, thus showing that nothing had dissolved in the HCl.

P. 43, N. 1: *Reactions between* $HClO_3$ *and* HCl.—See Schacherl (*Liebig's Ann. Chim.*, 1876, clxxxii., 193); Bray (*Zeit. Anorg. Chem.*, 1906, xlviii., 242).

P. 43, N. 2: *Non-existence of* $AsCl_5$.—See Smith and Hora (*Journ. Am. Chem. Soc.*, 1904, xxvi., 632). For earlier references, see Baskerville and Bennet (*Journ. Am. Chem. Soc.*, 1902, xxiv., 1070).

Non-volatility of Arsenic Acid from HCl *Solution.*—2·0 grms. As as As_2O_5, containing a small amount of As_2O_3, were dissolved in 20 cc. HCl (1·20), and distilled until only half the volume remained in the flask; 10 cc. more of HCl (1·20) were added, and the solution distilled as before; and this operation was repeated several times; the distillates were collected in separate portions of cold water, and saturated with H_2S; in the first distillates yellow precipitates appeared at once, which decreased in amount from about 15 mgrms. As in the first distillate to about 0·5 mgrm. As in the fifth. (This was evidently due to the As_2O_3 present as impurity). These solutions were filtered, and the filtrates treated at 90° with H_2S for several minutes; very little, if any, precipitate was obtained, showing that arsenic in the higher state of oxidation was practically absent. From later distillates precipitates containing about 0·5 mgrm. As separated quickly with H_2S in the cold, and no further precipitate separated when the solutions were heated and treated with H_2S. Thus, even from this concentrated solution of arsenic acid in the presence of concentrated HCl only a trifling amount of arsenic volatilised. Since the higher halogen compound of an element is in general more volatile than the lower, it is therefore highly probable, from the above result, that $AsCl_5$ is not present even in concentrated HCl solution.

P. 43, N. 3: *Non-Influence of Mercury, Antimony, or Tin on the Test for Arsenic with* $MgCl_2$.—Two mgrms. Hg as $HgCl_2$, 2 mgrms. Sn as $SnCl_4$, 2 mgrms. Sb as Sb_2S_3 were treated in separated experiments according to the procedure; with mercury a precipitate was obtained with NH_4OH, and the filtrate when acidified with HCl and treated with H_2S gave no precipitate; with tin and antimony no permanent precipitate formed in the NH_4OH solution, nor was one formed with $MgCl_2$ and NH_4Cl.

P. 43, N. 4: *Delicacy of Test for Arsenic.*—0·5, 1, and 2 mgrms. As as H_3AsO_4 were treated in separate experiments according to P. 43, the final volume being in each case about 5 cc.; with 2 mgrms. the $MgNH_4AsO_4$ precipitate appeared immediately upon shaking; with 1 mgrm., after gentle stirring; and with 0·5 mgrm., slowly after rubbing with a glass rod for a minute or two.

*P. 43*a*, N. 2: *Action of* KI *on* K_2PtCl_6.—To 5 mgrms. Pt as H_2PtCl_6 were added 10 cc. water and a few drops KI solution; a deep red solution resulted. Five cc. CS_2 were added, and the mixture shaken; the water layer remained dark red, and the CS_2 solution was coloured slightly, owing to the presence of a trace of iodine. The water layer was shaken with a fresh portion of CS_2; this time the CS_2 layer was colourless, thus proving that only an insignificant quantity of iodine was present, and therefore that the platinic compound is not reduced. To the solution some H_2SO_3 solution was added; the colour of the solution changed at once to a pale yellow.

*P. 43*b*, N. 1: *Action of Oxalic Acid on Solutions of Chlorauric, Selenous, Tellurous, and Molybdic Acids.*—Two mgrms. Au as $AuCl_3$ were dissolved in one experiment in a dilute HCl solution containing about 0·5 grm. $H_2C_2O_4$, in a second one in a dilute solution of NH_4OH and $(NH_4)_2C_2O_4$, and the solutions were evaporated to 3 to 4 cc.; no precipitate separated in either case. The solutions were then evaporated almost to dryness to expel the excess of HCl and of NH_4OH, were diluted to about 15 cc., and again boiled; a purple precipitate of gold quickly appeared in both cases. In another experiment 0·5 mgrm. Au as $AuCl_3$ was added to 10 cc. of a dilute $(NH_4)_2C_2O_4$ solution which had been made slightly acid with $H_2C_2O_4$, and the solution was heated to boiling; a purple precipitate of gold separated.

Five mgrms. Au as $AuCl_3$ were treated according to the procedure; a precipitate of gold appeared quickly, and continued to separate for two or three minutes. After about five minutes the gold was filtered off, and the filtrate again digested for several minutes on the steam-bath; no further precipitate of gold separated.

Fifty mgrms. Se as H_2SeO_3, 50 mgrms. Te as H_2TeO_3, and 50 mgrms. Mo as $(NH_4)_2MoO_4$ were treated in separate experiments by *P. 43*b*; in the case of tellurium a white precipitate separated from the $H_2C_2O_4$ solution on evaporation, but it dissolved readily on adding HCl; in the other two experiments no precipitate formed, and no colour change was noticed.

*P. 43*c*, N. 1: *Action of* H_2SO_3 *on* H_2SeO_3.—One mgrm. Se as SeO_2 in 10 cc. HCl (1·15) was saturated with SO_2 gas at room temperature; a red precipitate appeared at once, and continued to increase slowly. After five minutes the solution was filtered, and the filtrate allowed to stand; it remained clear. The experiment was repeated, except that the solution was saturated at 90°; a reddish precipitate appeared at once, but it changed rapidly to a very compact nearly black precipitate that collected at the bottom of the test tube. The first experiment was repeated with 0·5 mgrm. Se; a considerable red precipitate separated within five minutes.

*P. 43*c*, N. 2: *Action of* H_2SO_3 *on* H_2TeO_3.—100 mgrms. Te as TeO_2 were dissolved in separate experiments in 10 cc. HCl (1·20), in 10 cc. HCl (1·20), and 5 cc. water, and in 20 cc. HCl (1·12). Each solution in a test-tube was saturated with SO_2 gas, was allowed to stand five minutes, and then placed in a steam-bath at 100° for fifteen minutes; no precipitate of tellurium was formed in any case. Enough water was added to make the volume 30 to 40 cc.; a black precipitate of tellurium appeared at once.

In each of eight test-tubes were placed 0·5 mgrm. Te as TeO_2 and 25 cc. saturated H_2SO_3 solution. To the first of these were added 3 cc. 40 per cent HCl, to the second 4 cc., to the third 5 cc., and so on up to the eighth, which contained 10 cc.; the tubes were then all heated in a steam-bath; those with 3 and 4 cc. HCl gave scarcely any precipitate; in the others the quantity of precipitate increased with the increase of acid up to 7 cc., and then decreased steadily with further increase in the amount of HCl.

*P. 43*d*, N. 1: *Action of* KI *and of* KI + H_2SO_3 *on Tellurium Solutions.*—For the formation of TeI_4 in the reaction between H_2TeO_3 and KI, see Gooch and Morgan (*Am. Journ. Sci.*, 1896, [4], ii., 271). For the formation of K_2TeI_6, see Wheeler (*Am. Journ. Sci.*, 1893, [3], xlv., 267). For its deep red colour, see Norris and Fay (*Am. Chem. Journ.*, 1900, xxiii., 109).

To prove that tellurium itself and not an iodide of it is precipitated by H_2SO_3 and HI, 20 mgrms. Te as TeO_2 were dissolved in 10 cc. HCl (1·12) and 1 mgrm. I as KI, and a little solid Na_2SO_3 were added; a large black precipitate formed slowly. This was filtered off after half-an-hour, the filtrate was diluted to 20 cc., and to it were added a few drops KI solution and a little solid Na_2SO_3; a black precipitate estimated to contain only 1 to 2 mgrms. Te

resulted. The experiment was repeated, except that the mixture was allowed to stand over night before filtering; only about 0·2 mgrm. Te remained in solution.

To determine the proper concentration of HCl for the complete precipitation of the tellurium, a few drops of KI solution were added to solutions containing 0·5 mgrm. Te as TeO_2 dissolved in 10 cc. HCl (1·20), in 15 cc. HCl (1·15), in 20 cc. HCl (1·12), and in 30 cc. HCl (1·06), respectively; a deep red colour resulted in each case, but was less intense in the most concentrated and in the most dilute HCl than in the other two solutions. A crystal of Na_2SO_3 was added to each solution; no change was observed in the three more concentrated HCl solutions, but a black precipitate of tellurium formed in the most dilute solution. In another experiment 0·1 mgrm. Te was dissolved in 20 cc. HCl (1·06), and a drop of KI and a crystal of Na_2SO_3 added; a black precipitate resulted.

Fifty mgrms. Te as TeO_2 were treated according to the procedure, and the precipitated tellurium filtered off after five minutes; the filtrate had a strong odour of SO_2, but no more tellurium separated in half-an-hour, even when a little KI was added.

*P. 43*d*, N. 2: *Action of* HI *on* H_2SeO_3.—See Norris and Fay (*Am. Chem. Journ.*, 1900, xxiii., 109).

*P. 43*d*, N. 3: *Action of* HI *on* H_2MoO_4.—To separate solutions of 50 mgrms. Mo as MoO_3 in 10 cc. HCl (1·20) and in 20 cc. HCl (1·12) a few drops of KI solution were added; iodine was slowly liberated in both cases, but more rapidly in the more strongly acid solution.

*P. 43*e*, N. 2: *Action of Zinc and* KCNS *on* H_2MoO_4.—To 1 mgrm. Mo as MoO_3 dissolved in 20 cc. HCl (1·06) in a test-tube were added a crystal of KCNS and some granules of zinc; a brilliant red colour appeared very quickly, and remained unchanged for about five minutes; the colour slowly changed to yellow, and then faded until after about half-an-hour the solution was nearly colourless. The experiment was repeated, except that the KCNS was not added until after the action of the zinc had continued for fifteen minutes; a yellow colour resulted. The experiment was repeated, except that the KCNS was added after about an hour; the solution remained colourless.

For the composition of the red compound produced with KSCN and zinc, see Sand and Burger (*Ber.*, 1905, xxxviii., 3384; 1906, xxxix., 1761).

P. 44, N. 1 and 2: *Action of* H_2S *on* H_3AsO_4 *Solutions.*—See McCay (*Am. Chem. Journ.*, 1888, x., 459). Brauner and Tomicek (*Journ. Chem. Soc.*, 1888, liii., 145). Usher and Travers (*Journ. Chem. Soc.*, 1905, lxxxvii., 1370).

P. 45, N. 1: *Separation of Antimony and Tin by* H_2S.—Known amounts of Sb and Sn as chlorides were added to an ammonium polysulphide solution, and precipitated as Sb_2S_5 and SnS_2 with HCl; the precipitates were dried by suction, and digested with 10 cc. HCl (1·20) at 90° for ten minutes in a 50 cc. conical flask. Each solution so obtained was diluted to a known volume, and treated with H_2S just below the boiling-point. The volume of the diluted solution at which the precipitation of Sb_2S_3 was nearly or quite complete, and that at which the precipitation of SnS_2 began, and became considerable are given in the following table:—

Experiment No.	Sn.	Sb.	Volume of solution at which precipitation of antimony was—		Volume of solution at which precipitation of tin—	
			Nearly complete.	Complete.	Began.	Was considerable
	Mgrms.	Mgrms.				
1	500	0	..	..	50	60
2	500	0	..	..	60	70
3	400	1	40	50	60	70
4	500	1	..	50	60	70
5	500	1	..	55	60	70
6, 7	500	200	40	50	60	70
8	10	500	40	50	..	..
9	200	200	..	50	..	..
10	0	1	..	55	..	..

In Experiment No. 1 a slight yellow precipitate of SnS_2 appeared in testing for antimony, but a good blank was obtained in No. 2. In Experiment 4 an orange-red precipitate of Sb_2S_3 was obtained; in Experiment 5 a dark coloured precipitate, which gave a good confirmatory test for antimony. In Experiment 10 the Sb_2S_3 precipitate did not separate until the last 5 cc. of water were added.

P. 45, N. 2: *Precipitation of* CuS *and* HgS *from* HCl *Solution.*—One mgrm. Cu and 0·5 mgrm. and 4 to 5 mgrms. Hg as chlorides were added in separate experiments to 10 cc. HCl (1·20) and 40 cc. H_2O, and the solutions were heated to boiling, and saturated with H_2S at 90°; in the first two cases light grey precipitates formed slowly, which on the filter appeared to be black; in the last case a black precipitate. The precipitates were filtered out, the solutions diluted and treated with H_2S; in the mercury experiments they gave no precipitates, but in the case of Cu a very slight precipitate formed.

P. 46, N. 1: *Influence of Copper and Mercury on the Reduction Test for Antimony.*—One and 2 mgrms. Hg as HgS, and 1 and 2 mgrms. Cu as CuS were treated in separate experiments according to P. 46; the mercury separated on the platinum as a grey loosely adhering film, the copper as a red metallic, firmly adhering deposit, which could not be mistaken for antimony.

The experiments were repeated in the presence of 0·5 and 1 mgrm. Sb; characteristic black deposits of Sb were obtained.

P. 46, N. 2: *Behaviour of Arsenic and Tellurium in the Reduction Test for Antimony.*—One, 4, and 10 mgrms. As as H_3AsO_4, and 0·5 mgrm. Te as H_2TeO_3 were treated in separate experiments according to P. 46; with the 10 mgrms. As and with the tellurium black deposits on the platinum were obtained, which dissolved readily in a normal cold alkaline solution of NaOCl; no deposit of arsenic was obtained with the 1 or 4 mgrms. As. It is therefore improbable that a black deposit of arsenic will ever be obtained in an actual analysis, since only very small amounts will be dissolved in the HCl treatment (P. 42).

Insolubility of Sb *in* NaOCl.—One mgrm. Sb precipitated on platinum-foil by the action of HCl and Sn was treated in the cold for five to ten minutes with a normal alkaline NaOCl solution; no change took place.

P. 47, N. 1: *Effect of Temperature on the Precipitation of* SnS_2.—A solution of 1 mgrm. Sn as $SnCl_4$ in 10 cc. HCl (1·20) was successively diluted with portions of water, and saturated with H_2S at 90° after each dilution; a precipitate formed only when the volume of the solution had become 110 to 120 cc. The experiment was repeated several times, except that the solutions were saturated for 5 to 10 minutes with H_2S at 20°; a precipitate formed when the volume became 60 to 70 cc.

P. 47, N. 2: *Delicacy of Confirmatory Test for Tin.*—0·5 Sn as $SnCl_4$ was treated in several experiments according to P. 47; in all cases a precipitate of SnS_2, and in most cases one of Hg_2Cl_2, was obtained.

Tetramethyl Dioxyacetone.—Louis Henry.—When ethyl mesoxalate acts on magnesium methyl bromide in ethereal solution in the proportion of one molecule of the former to five of the latter compound, the product of the reaction is a white substance crystallising in needles. It is insoluble in water, easily soluble in alcohol and ether, melts at 117—118°, and boils without decomposition at 238—240° under ordinary pressure. This substance is found by analysis and by the cryoscopic determinations of the molecular weight to be tetramethyl dioxyacetone, $(CH_3)_2=C(OH)-CO-C(OH)=(CH_3)_2$. It is noteworthy that, in spite of the presence of sufficient organo-metallic substance, the ketonic group, $>CO$, is not attacked. The melting- and boiling-points of this compound agree with those which would be assigned to it *à priori* if the effect of the intercalation of the ketone group were calculated.—*Comptes Rendus*, cxliv., No. 22.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, June 6th, 1907.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

MESSRS. A. T. Cameron, G. Fowles, S. W. Smith, and J. W. Yates were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frank Buckney, B.A., 51, Highbury Park, N.; William Hay, Holton House, Beverley Road, Hull; George Joseph Saunders, B.E., School of Mines, Charters Towers, Queensland, Australia; David Willott, B.Sc., Rosedale, Thorncroft Road, Sutton, Surrey; Hubert Arthur Wootton, B.A., B.Sc., 20, Great College Street, Westminster, S.W.

Of the following papers, those marked * were read:—

*117. "*The Relation between Absorption Spectra and Chemical Constitution.* Part VII. *Pyridine and some of its Derivatives.*" By FRANK BAKER and EDWARD CHARLES CYRIL BALY.

The authors have made a spectroscopic examination of pyridine and its substitution products, with the object of determining the influence of the nitrogen atom and also the constitution of the pyridones. It was shown how the nitrogen atom tends to restrain the motions of the ring, this restraint being very much lessened by the addition of acid to the solutions. A very similar effect is produced by the substitution by chlorine, inasmuch as the basicity of the nitrogen is thereby considerably reduced.

In the case of the oxypyridines, the α- and γ-compounds were shown to be true pyridones, whilst the β-isomeride possesses the hydroxylic configuration.

*118. "*The Interaction of Methylene Chloride and the Sodium Derivative of Ethyl Malonate.*" By FRANK TUTIN.

The reaction which takes place when methylene chloride is heated with an alcoholic solution of the sodium derivative of ethyl malonate has been studied, and the following three crystalline by-products resulting from the condensation were examined.

1. A sodium salt crystallising from alcohol in yellow leaflets.

2. An *acid* crystallising in needles, which melt at 132°.

3. An *acid* obtained in small needles, which are insoluble, or nearly so, in all solvents.

The yellow sodium salt was obtained by Perkin and Prentice (*Trans.*, 1891, lix., 991), but was not further examined by them. It has the formula $C_{15}H_{21}O_8Na$, and yields a liquid *acid*, $C_{14}H_{21}O_6{\cdot}CO_2H$, which gives a violet coloration with ferric chloride. On hydrolysis, this acid first gives an *acid* melting at 305°, but when completely hydrolysed, yields a *tetracarboxylic acid*, $C_6H_8(CO_2H)_4$ (m. p. 138—139°). The latter compound, although melting at the same temperature as *cis-cyclo*hexane-1:2:4:5-tetracarboxylic acid, is not identical with it.

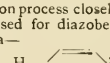
The substance melting at 132° possesses the formula $C_{18}H_{24}O_6(CO_2H)_2$, and, on hydrolysis, yields an *acid* melting at 306°.

The insoluble substance is hydrolysed by sodium carbonate, giving a *sodium* salt, $C_{32}H_{35}O_{20}Na_3{,}6H_2O$, crystallising in white needles; the corresponding *potassium* salt is insoluble and anhydrous. The *acid*, $C_{29}H_{35}O_{14}(CO_2H)_3$, obtained from these salts crystallises in leaflets melting at 200°.

*119. "*The Constitution of the Diazo-compounds.*" By JOHN CANNELL CAIN.

None of the formulæ hitherto proposed for the diazo-salts can account for the great ease with which such compounds lose their diazo-nitrogen. Nitrogen attached to the benzene ring, as, for example, in the case of aniline, is readily eliminated only by oxidation, and Ostrogowich and Silbermann have recently shown that in this process aniline probably assumes the tautomeric form—

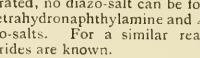
As the diazotisation process closely resembles this reaction the author proposed for diazobenzene salts (chloride) the quinonoid formula—



this bears much analogy to the formula of quinonechloroimide, which also loses nitrogen on boiling with water.

The new formula explains why, in compounds where the atom in the para-position to the amino-group is already saturated, no diazo-salt can be formed; thus, for example, *ac*-tetrahydronaphthylamine and 4-aminoquinoline yield no diazo-salts. For a similar reason no aliphatic diazochlorides are known.

The corresponding formula for the diazohydroxide may, unlike the chloride, give rise to two tautomeric forms:—



the latter of which represents the constitution of the normal or *syn*-diazo-compounds, and is closely related to the formula for the *iso*- or *anti*-compounds:—

As these formulæ fully explain the reactions of the diazo-compounds the stereo-chemical theory is rendered unnecessary.

The following recommendations as to nomenclature were suggested:—

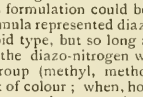
i. The word "diazonium" should be retained for the diazo-salts.

ii. The normal or *syn*-metallic diazo-compounds should be called normal diazo-oxides or diazo-oxides.

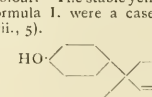
iii. The *iso*- or *anti*-compounds should be called *iso*-diazo-oxides.

DISCUSSION.

Dr. MORGAN said that the retention of the quinquivalency of the salt forming nitrogen atom, and the representation of the mobility of the diazo-group N_2 by means of the doubly linked attachment to the aromatic nucleus, were both strong arguments in favour of the new formula for diazonium salts. It must, however, not be forgotten that other types of diazo-derivatives, the diazoamines and the acyl-*p*-diazoimides, for example, also readily give up their diazo-nitrogen, and it still remained to be seen whether this formulation could be extended to those cases. The new formula represented diazonium salts as substances of a quinonoid type, but so long as the radicle in the para-position to the diazo-nitrogen was hydrogen or a simple saturated group (methyl, methoxyl, &c.) there was no development of colour; when, however, this hydrogen was replaced by a complex aromatic group then the compound exhibited colour. The stable yellow diazo-salts having the general Formula I. were a case in point (Cain, *Trans.*, 1905, lxxxvii., 5).



I.



II.

Having been engaged for some time in the investigation of compounds of this nature, he hoped, in conjunction with Mr. Wootton, to bring forward at the next meeting a complete series of coloured stable diazo-salts (Formula II.) derived from *p*-aminobenzo-α-naphthalide. A formula such as that advocated by Dr. Cain afforded a satisfactory explanation of the properties and reactions of these substances.

Dr. Hewitt drew attention to the coloured diazonium salts which had been obtained by different chemists. Some of the earliest to be isolated were those derived from *p*-semidine bases; these were not merely coloured, but Jacobson found that they were remarkably stable to heat. The diazonium salts prepared by Dr. Cain and Dr. Morgan were coloured and stable, and like Jacobson's compounds could be represented with a true quinonoid structure.

Dr. Lapworth pointed out that if, as this ingenious formulation indicated, one of the nitrogen atoms in the diazo-group was attached to the carbon atom in the para-position to that linked to the other nitrogen atom, it had to be assumed that the new carbon-nitrogen linking was very much more unstable than that which represented the normal link between the diazo-group and the benzene nucleus. Yet the former was represented as a single bond, whilst a double one was assumed in the latter case to account for its instability. Had Dr. Cain any explanation of the fact that during the changes of diazo-compounds nitrogen had never been found at the point where his formula suggested it should, at least occasionally, be discovered?

Dr. Cain, in reply to Dr. Lapworth, pointed out that the linking in the group N·CH was usually a very unstable one, and in the present case was largely influenced by the condition of the linkings in the benzene nucleus.

120. "*Dibromoaminoazobenzene.*" By John Theodore Hewitt and Norman Walker.

A dibromoaminoazobenzene, produced by the action of bromine on an aqueous alcoholic solution of aminoazobenzene, has been described by Berju (*Ber.*, 1884, xvii., 1403), who gives the melting-point as 152°, and has not determined the constitution of the compound. The present authors find that the action of bromine on an acetic acid solution of aminoazobenzene in presence of sodium acetate gives benzeneazo-*oo* dibromoaniline, m. p. 168°. This forms the chief constituent of the product obtained by Berju's method. The *diacetyl* derivative melts at 137°, the *dibenzoyl* derivative at 229°. The constitution was determined by reduction with sodium hyposulphite, the 2 : 6-dibromo-1 : 4-phenylenediamine of m. p. 138° (E. Noelting, E. Grandmougin, and O. Michel, *Ber.*, 1892, xxv., 3334) being isolated.

121. "*Phenol* p-*Sulphoxide.*" By Samuel Smiles and Alexander William Bain.

The authors described the preparation of *phenol* p-*sulphoxide*, and showed that its properties differ widely from those assigned by Schall and Uhl (*Ber.*, 1892, xxv., 1893) to the substance obtained by the action of fused alkali hydroxide on the dye-stuff rubbadin, and to which they attributed the same constitution. The condensation of phenol *p*-sulphoxide with salicylic acid yields *di-p-hydroxy-phenylsalicylthetine*.

122. "p-*Cresol Sulphoxide and Sulphide.*" By Samuel Smiles and Thomas Percy Hilditch.

These substances were obtained during an investigation of the action of dehydrating agents on ortho-hydroxysulphoxides. p-*Cresol sulphoxide* is formed by the interaction of *p*-cresol, aluminium chloride, and thionyl chloride. It crystallises in needles, which melt at 191°, and are soluble in alcohol or hot water; it dissolves in strong sulphuric acid with a deep blue colour, but, unlike the other hydroxy-sulphoxides which have been prepared, this colour is not discharged by the addition of a phenolic ether (Smiles and Le Rossignol, *Trans.*, 1906, lxxxix., 701). When the blue solution is mixed with water a pink solid is precipitated. The same substance was obtained by boiling the sulphoxide with phosphoryl chloride; it is soluble in aqueous alkali hydroxide, and the yellow solution on shaking with benzoyl chloride yields a colourless benzoyl derivative. The substance also furnishes a platinichloride. On account of the amorphous character of these compounds the investigation has been abandoned.

Dibenzoyl-p-cresol sulphoxide melts at 173°.

p-*Cresol sulphide* was prepared by reduction of the sulphoxide; it crystallises from a mixture of acetic acid and water in colourless needles, which melt at 101—103°.

123. "*Molecular Weight of β-Naphthol in Solution in Solid Naphthalene.*" By Edgar Philip Perman and John Hughes Davies.

The vapour pressures of solid naphthalene, of β-naphthol, and of isomorphous mixtures of these substances, at 70°, were estimated by aspirating a known volume of air through a glass spiral containing the solid, and determining the loss of weight. The mean vapour pressures obtained were:—Naphthalene, 3·751 mm. of mercury; β-naphthol, 0·1134 mm.; solid solution of five parts of β-naphthol to 100 parts of naphthalene, 3·592 mm.; ten parts to 100, 3·476 mm.; fifteen parts to 100, 3·380 mm. The corresponding molecular weights calculated are 151, 175, and 194 respectively. It is concluded that in dilute solutions, β-naphthol has the same molecular weight as in the gaseous state, whilst it associates in more concentrated solutions.

124. "*Synthesis of Hexatriene Derivatives.*" (Preliminary Note). By Ida Smedley.

Experiments undertaken with the object of preparing a series of hexatriene derivatives by the elimination of chlorine from αα-dichloro-γ-alkyl-propylenes having led to unsuccessful results (*Proc.*, 1906, xxii., 158), the method adopted by Van Romburgh and Dorssen (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, viii., 565) for the preparation of the simplest member of the series, C_6H_8, was applied. The formate of dihydrocinnamoin was prepared; this readily resinifies, and does not therefore afford a convenient method of synthesis of the pure diphenylhexatriene, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C_6H_5$.

This hydrocarbon may, however, be obtained by the condensation of phenyl*iso*crotonic acid with cinnamaldehyde in the presence of acetic anhydride. From acetone or benzene solution, it is deposited in pale yellow crystals, melting at 194°. The dilute benzene solution exhibits a remarkable blue fluorescence.

125. "*The Reduction of Aromatic Nitro-compounds to Azoxy-derivatives in Acid Solution.*" By Bernhard Flurscheim and Theodor Simon.

According to a general rule, azo- and azoxy-compounds are formed when aromatic nitro-compounds are reduced in alkaline solution, but never in presence of free mineral acids. One of the authors has, however, previously shown (*Journ. Prakt. Chem.*, 1905, [ii.], lxxi., 497) that it is often possible to isolate the azoxy-compound in acid solution as well, sometimes even in theoretical yield, and that the above mentioned law must be abandoned.

It was, however, further necessary to determine the conditions which favour the formation of azoxy-products or prevent it. To render this possible, an exact separation of the substances, resulting from the reduction of nitro-compounds by means of stannous chloride and hydrochloric acid in alcoholic solution, had to be effected. To this end the first part of the present research has been devoted, and the authors have succeeded in separating quantitatively the products of reduction, namely, amines, aminophenols, azoxy- and aminoazoxy-compounds from each other and from the unattacked nitro-compounds.

With the help of these new methods, more than sixty reductions have been carried out, with varying quantities of acid, and under changing conditions. The following nitro-compounds have been used:—Nitrobenzene, *m*-dinitrobenzene, 2 : 4-dinitrotoluene, 4 : 6-dinitro-*m*-xylene, 1-chloro-2 : 4-dinitrobenzene, 1-bromo-2 : 4-dinitrobenzene, 3 : 5-dichloro 4-bromonitrobenzene, 2 : 4-dinitrodiphenyl amine, and *p*-nitrobenzaldehyde. The chief results may thus be briefly summarised:—

1. Reduction in acid, neutral, and alkaline solutions proceeds in accordance with Haber's hypothesis, nitroso- and hydroxylamino-derivatives being successively formed.

2. The formation of azoxy-compounds during reduction is due to a condensation of hydroxylamino- and nitroso-derivatives.

3. This condensation can only take place when the residual affinity of the tervalent nitrogen atom in the hydroxylamino-compound is not saturated.

4. Such saturation taking place, when salts are formed anything favouring dissociation of these salts, for instance, negative substituents in the nucleus, also favours condensation, whilst increasing quantities of acid tend to prevent it.

5. A diminution in the velocity of reduction favours condensation.

6. Ortho-substituents diminish the velocity both of reduction and condensation; these being opposite influences, the influence of ortho-substituents on the formation of azoxy-compounds varies with their nature, some favouring condensation (bromine, &c.), others tending to prevent it (methyl, &c.).

All the results can be depicted graphically, the percentage of azoxy-compounds produced forming for each substance a curve falling with increasing quantities of acid used. In the absence of ortho-substitution, nitro-compounds with strongly negative nucleus substituents yield curves running above those obtained with less negative radicles.

126. "*Action of Selenium and Tellurium on Arsine and Stibine.*" By FRANCIS JONES.

In continuance of his previous work (*Journ. Chem. Soc.*, 1876, 641), where it was shown that sulphur decomposes arsine and stibine in presence of light in accordance with the equation $2SbH_3+6S = Sb_2S_3+3H_2S$, the author has now investigated the action of these hydrides on the elements analogous to sulphur, namely, selenium and tellurium, in presence and absence of light, and at 100°.

The results are shown in the following table:—

Element.	Hydride.	Result.
	a. *In Sunlight.*	
Sulphur	SbH_3	Reacts easily
Selenium	SbH_3	Reacts easily
Tellurium . ..	SbH_3	Reacts
Sulphur	AsH_3	Reacts slowly
Selenium	AsH_3	Reacts
Tellurium . ..	AsH_3	Reacts
	b. *At* 100°.	
Sulphur	SbH_3	Reacts slowly
Selenium	SbH_3	Reacts slowly
Tellurium . ..	SbH_3	Reacts very slowly
Sulphur	AsH_3	Reacts slowly
Selenium	AsH_3	No action
Tellurium . ..	AsH_3	No action
	c. *In the Dark.*	
Sulphur	SbH_3	No action
Selenium	SbH_3	Reacts slightly
Tellurium . ..	SbH_3	No action
Sulphur	AsH_3	No action
Selenium	AsH_3	No action
Tellurium . ..	AsH_3	No action

It was previously shown that the facility of the decomposition of the hydrides increases with the rise in the molecular weight of these gases, phosphine being very slowly decomposed, arsine more rapidly, and stibine very rapidly. It is now found that the action of these hydrides on sulphur, selenium, and tellurium corresponds with the rise in the atomic weights of these elements, stibine being readily decomposed by sulphur, more slowly by selenium, and still more slowly by tellurium. An exception was noticed in the case of stibine, which acts on selenium even in the dark.

In the course of the investigation it was observed that arsine reacts with solution of lead acetate, producing a black precipitate, probably an arsenide of lead, the composition of which varied in different preparations.

127. "*The Double Nitrites of Mercury and the Alkali Metals.*" By PRAFULLA CHANDRA RAY.

Mercuric nitrite forms a series of double salts with the nitrites of potassium, sodium, and lithium in which one molecule of the former combines with 1, 1½, 2, 3, and 4 molecules of the latter.

128. "*Silver-mercuroso-mercuric Hydroxynitrates and the Isomorphous Replacement of Univalent Mercury by Silver.*" By PRAFULLA CHANDRA RAY.

When a solution containing mercuroso-mercuric nitrite and silver-mercuric nitrite is allowed to evaporate spontaneously, a series of silver-mercuroso-mercuric hydroxynitrates crystallises out. In each of these salts a part of the mercurous mercury is isomorphously replaced by silver.

129. "*The Molecular Weights of Amides in Various Solvents.*" (Preliminary Note). By ANDREW NORMAN MELDRUM and WILLIAM ERNEST STEPHEN TURNER.

In the course of an investigation into the molecular condition of typical amides in various solvents, the authors have found that the molecules of trichlorolactamide, of benzanilide, and of salicylamide are associated in benzene solution even at the boiling-point, and those of benzamide in benzene, in chloroform, and in acetone solution.

No case of association in alcohol solution has been discovered, acetamide, monochloroacetamide, and benzamide giving normal results. In the case of amides derived from stronger organic acids than these, the "molecular weights" in alcohol are abnormally low.

The results obtained with water as solvent are unexpected, association being found in at least three cases, acetamide, benzamide, and salicylamide.

130. "*Some Experiments on the Oxidising Action of Hydrogen Peroxide.*" (Preliminary Note). By WILLIAM HENRY PERKIN, jun.

During the course of researches on the constitution of brazilin and hæmatoxylin, the observation was made that certain of their derivatives, when treated with hydrogen peroxide (30 per cent) and acetic acid, were readily oxidised with the formation of new substances the investigation of which will, it is hoped, throw much light on the constitutions of these important natural colouring matters.

Thus, for example, *brazilein*, $C_{16}H_9O_2(OH)_3$, is under these conditions converted into a substance, $C_{16}H_{14}O_9$, which crystallises in brown needles, and *trimethylbrazilein*, $C_{16}H_9O_2(OMe)_3$, yields a colourless crystalline substance, $C_{19}H_{20}O_8$, which melts at 218° with decomposition. The detailed description of these and other similar oxidation experiments of brazilein and hæmatein is reserved for a subsequent communication.

Experiments of a more general nature seem to indicate that hydrogen peroxide may prove to be a reagent of considerable importance, especially in connection with analytical researches.

It appears, for example, to react readily with *aa*-diketones and generally with substances possessing quinonoid structure.

Benzil is readily attacked, when its suspension in a little acetic acid is mixed with hydrogen peroxide and warmed on the water-bath, and the product contains large quantities of benzoic acid and a pale yellow oil which has not yet been investigated.

When *phenanthrenequinone* (5 grms.) suspended in glacial acetic acid (15 cc.) and hydrogen peroxide (5 cc.) is heated at 90—95°, the crystals soon dissolve, and the solution, on dilution with water, deposits 5 grms. of pure diphenic acid, a method which is by far the most convenient for the preparation of this important acid.

Aurin, under similar conditions, is very readily attacked by hydrogen peroxide with formation of *p*-hydroxybenzoic

acid and benzoquinone. Obviously the aurin is, in the first place, oxidised to *p*-hydroxybenzoic acid and quinol,—

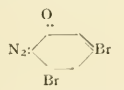
$$(C_6H_4{\cdot}OH)_2C{:}C_6H_4{:}O + 2H_2O_2 = \\ = C_6H_4(OH){\cdot}CO_2H + 2C_6H_4(OH)_2,$$

and the latter is then further oxidised to benzoquinone. It will be shown, in a later communication, that this decomposition is of importance in connection with the determination of the constitution of brazilein and hæmatein. The special value which appears to attach to hydrogen peroxide lies in the fact that it can be employed to oxidise phenolic substances, like brazilein and aurin, without the usual and often very laborious routine of protecting the hydroxyl groups by methylation. Experiments are in progress with the view of determining the special conditions under which hydrogen peroxide may be employed with success. The presence of acetic acid appears to be generally advantageous, but other solvents may be employed, and, in some cases, the oxidation of phenolic substances has been found to proceed well in alkaline solution.

131. "*Action of Hydroxylamine on o-Benzoquinonediazides* (*o-Diazophenols*). 3 : 5-*Dibromo-o-azoiminobenzoquinone* (4 : 6-*Dibromo-2-Hydroxyphenylazoimide*)." (Preliminary Note). By Kennedy Joseph Previté Orton, William Charles Evans, and Emrys Morgan.

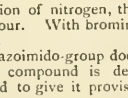
The simple means of preparing the benzoquinonediazides, especially the halogen-*o*-benzoquinonediazides from the 5-trihalogendiazonium salts of weak acids (Orton, *Trans.*, 1903, lxxxiii., 796), a reaction in which a halogen atom is replaced by a hydroxyl group, has permitted of a detailed study of the behaviour of these substances with a number of reagents. The recent appearance of a paper by Forster and Fierz on "Aromatic Azoimides" (*Trans.*, 1907, xci., 855), in which is described the preparation of *p*-hydroxyphenylazoimide from *p*-diazophenol and hydroxylamine, shows that it is advisable to make a preliminary announcement of one of the authors' results.

3 : 5-Dibromo-*o*-benzoquinonediazide,—



(Orton, *loc. cit.*), reacts very readily with hydroxylamine in alcohol solution, the reaction being completed if the hydrogen chloride of the hydroxylamine hydrochloride is replaced by a weak acid or neutralised by a base. On adding water to the resulting alcoholic solution, the *azoimide*, the yield of which is quantitative, separates in yellowish brown needles melting at 98°, the molten material decomposing slowly a few degrees above the melting-point. The azoimide is readily soluble in all organic solvents except light petroleum, and is slightly soluble in water, to which it imparts a bright yellow colour. It has a decided acid character, dissolving in solutions of alkali hydroxides and carbonates. In anhydrous solvents, it also appears to combine directly with hydrogen chloride. The azoimide dissolves in sulphuric acid with the evolution of nitrogen, the solution acquiring a deep magenta colour. With bromine it yields a tetrabromoaminophenol.

Inasmuch as the azoimido-group does not in itself confer colour, whilst this compound is deeply coloured, the authors are inclined to give it provisionally a quinonoid structure, thus:—



3 : 5-Dibromo-2-nitro-*p*-benzoquinonediazide and 4-bromo-*o*-naphthaquinonediazide (Orton, *loc. cit.*) react similarly with hydroxylamine.

132. "*Oxime Formation and Decomposition in presence of Mineral Acids.*" By Arthur Lapworth.

The conversion of stable hydroximido-compounds into the corresponding ketones or aldehydes is, as a rule, to be effected by the use of hydrochloric acid in presence of formaldehyde. *iso*Nitrosocamphor, for example, gives an excellent yield of camphorquinonine, and even camphoroxime may be partially converted into camphor by this method, which appears to be the most general hitherto discovered. The formaldehyde is converted into formic acid in the process, while the nitrogen of the oxime appears mainly as ammonium chloride.

The hydrolytic action of mineral acids on oximes appears to be a reversible one, which is possibly, in part, the explanation of the favourable influence of the formaldehyde in the above instances. When hydroxylamine, formaldehyde, and concentrated hydrochloric acid are heated together, formic acid, ammonium chloride, and methylammonium chloride are formed. When benzaldehyde is substituted for formaldehyde, benzaldoxime, and, sometimes, benzonitrile, are formed. Camphorquinone yields camphorimide, and camphor gives campholenonitrile.

133. "*Note on the Constituents of the Seeds of the Para Rubber Tree* (Hevea brasiliensis)." By Wyndham Rowland Dunstan.

The kernels of the seeds of the Para rubber tree (*Hevea brasiliensis*) were examined at the Imperial Institute in 1902, and found to contain about 50 per cent of a fixed oil, having a specific gravity 0·9302 at 15°, saponification value 206·1, and iodine value 128·3. Like linseed oil, to which it bears considerable resemblance, this oil "dried" to a transparent varnish on exposure to air, and will probably be of commercial value for the same purposes. In the future there is likely to be an enormous production of these seeds which will not be required for planting, and their commercial utilisation is therefore a matter of importance (*Bull. Imp. Inst.*, 1903, i., 156, and 1904, ii., 22).

The seed kernels, when ground with water, evolved small quantities of hydrocyanic acid and acetone, whence it appears that a cyanogenetic glucoside is present, similar to if not identical with the phaseolunatin first obtained from the beans of *Phaseolus lunatus* (Dunstan and Henry, *Proc. Roy. Soc.*, 1903, lxxii., 285), and subsequently isolated from flax and cassava (Dunstan, Henry, and Auld, *Ibid.*, 1906, lxxviii., 145).

A mixture of enzymes was prepared from the seeds which possessed the property of hydrolysing the oil present and also olive oil. These enzymes probably include, besides a lipase-like enzyme, one capable of decomposing the cyanogenetic glucoside, since the kernels yield hydrocyanic acid by mere contact with water. The nature of the fixed oil of the cyanogenetic glucoside and of the enzymes is being fully investigated.

Van Romburgh has shown (*Ann. Jard. Bot. Buitenzorg*, 1899, xvi., 15) that the leaves of *Hevea brasiliensis* also yield hydrocyanic acid and acetone when crushed with water, and Harrison has recorded the production of hydrocyanic acid under similar conditions from the seeds of the related species *Hevea panciflora* and *Hevea confusa* (*Rep. Govt. Lab. Brit. Guiana*, 1896-1902, Part II., p. 11).

It is hoped that sufficient material will be obtainable to enable the question to be settled as to whether these related plants, as well as *Hevea brasiliensis*, contain phaseolunatin, as seems probable.

Society of Chemical Industry.—H. M. the King has been pleased to grant a Charter of Incorporation to this Society, which was founded in 1881 to promote the application of chemical science to arts and manufactures.

NOTICES OF BOOKS.

Cyaniding Gold and Silver Ores. By H. Forbes Julian and Edgar Smart, A.M.I.C.E. Second Edition. London: Charles Griffin and Co., Ltd. 1907.

In the first edition of this treatise the authors collected from all sources information relating to the theory of the cyanide process and its practical application, and thus produced a book which for the first time gave a satisfactory survey of the whole process in all its aspects. The second edition is a no less valuable work, which managers of cyanide works who have either not the time or else lack the opportunity to refer to original publications, will find gives them sufficient information to enable them to understand thoroughly both practice and theory. All recent developments and innovations in the process are discussed with the introduction of as little mathematics as possible, and there can be no doubt that the book must rank as one of the authoritative treatises on the subject; it explains the process on a scientific basis, eliminating rule-of-thumb methods and urging the necessity of a thorough understanding of all the principles involved.

The Book of Receipts. (Beasley). Re-written by E. W. Lucas, F.I.C., F.C.S. Eleventh Edition. London: J. and A. Churchill. 1907.

This book is based upon the last reprint of Beasley's "Druggists' Receipt Book," but contains much new matter, for instance short accounts of the examination of potable waters, and the analysis of milk, &c., are now included, and many volumetric and other tables have been added. The book contains a Veterinary Materia Medica with prescriptions for the commonest ailments of animals, and a pharmaceutical formulary giving details of the preparation of many articles of domestic use and also proprietary articles. In addition, a photographic formulary gives directions for making up developing, toning, and fixing solutions, while much miscellaneous information which may be found useful by chemists, druggists, and manufacturers is included.

The Cinematograph in Science, Education, and Matters of State. By Charles Urban, F.Z.S. London: Charles Urban Trading Co., Ltd.

The object of this pamphlet is to call attention to the great value of the cinematograph as an educational instrument, which should be regarded as an indispensable possession by all well-equipped teaching institutions. The cinematograph, provided that the pictures are well chosen by experts, has not the limitations of lantern slides and is a more valuable means of imparting instruction. The Charles Urban Trading Company have prepared many subjects of scientific and general interest, and in this short account of their resources explain how the instrument may be used to teach geography, in which its great importance will at once be obvious, history, and some branches of technical and industrial science. In matters of state the cinematograph may be used as an aid to the recruiting agent, and also to take records in military and naval manœuvres, while in science its value in operative surgery cannot be called in question, and in the course of a few years important developments in its use may be expected.

Nitrate Facts and Figures. Compiled by A. F. Brodie James, F.S.S. London: Fredc. C. Mathieson and Sons. 1907.

With a view to helping the investor to compute upon a sound basis the actual value of the shares of various nitrate companies, and the return he may expect if he puts his money in them, the compiler of these tables has brought together details as to the companies now in existence and their directors, tabulating the date of formation, the capital, dividend, and reserve funds, together with information relating to the output, &c. Possibly the publication of the report, which places the English public upon an equality with that of South America as far as access to details is concerned, will act beneficially upon the development of nitrate companies here, by giving investors a feeling of security, or at any rate a knowledge of the risks they are running.

The Workmen's Compensation Act, 1906. Handy Notes for Employers. By A. F. O. Walbrook. London: Law, Car, and General Insurance Corporation, Limited.

These notes upon the Workmen's Compensation Act, 1906, endeavour to throw some light upon the interpretation of an act which, in the author's opinion, is full of difficulties like its predecessors. Without laying any claim to be an exhaustive discussion of the provisions of the act, the notes show clearly what persons are entitled to compensation, and what accidents carry compensation, also the amount which the employer may be called upon to pay in the event of the partial or total disablement or death of an employee. The author emphasises the far reaching effects which the act may have, and the notes will help employers to decide what their liabilities are, and also what should be the provisions of a satisfactory insurance policy.

Post's Chemisch-Technische Analyse. ("Post's Technical Analytical Chemistry"). Edited by Dr. Bernard Neumann. Vol. I., Part II. Braunschweig: Friedrich Vieweg und Sohn. 1907.

This analytical handbook gives a summary of laboratory as well as technical methods of investigating the raw material and products of various industries, and as a wide view is taken of the subject the book has a value much above that of a mere laboratory guide; in fact, it may be regarded as a valuable work of reference for the library shelves, as well as a trustworthy practical book. The different sections have been written by authors whose names are in all cases a sufficient guarantee of the accuracy and completeness of the parts for which they are individually responsible. The second part of volume I. contains a section on Illuminating Gas, written by Dr. Julius Becker, in which he discusses the analysis of coal and of gas, and also the determination of the illuminating power of the latter by photometric methods. The examination of calcium carbide and acetylene is treated by Prof. J. H. Vogel, and petroleum, paraffin, and allied substances by Prof. Engler and Dr. Ubbelohde. The last section of the book, written by Dr. Fahrion, is devoted to the fats and fatty oils, glycerin, soaps, and candles, and gives short accounts of the most satisfactory methods of analysing and examining these products for adulterations and impurities. Throughout the book the illustrations are very clear, and since the dimensions are usually indicated they should give real assistance in setting up apparatus in the most convenient form and size.

L'Énergie. ("Energy"). By Alphonse Cruz. Second Edition. Amiens T. Jeunet. 1907.

In this pamphlet the author discusses and criticises at some length the theories advocated in G. le Bon's book, "L'Evolution de la Matière," devoting his attention more especially to the hypothesis that energy and matter are two different aspects of the same thing. He suggests that as energy without mass and movement is impossible, and as these things are the two essential properties of matter, matter and energy are not different manifestations of the same thing, but are actually identical, the only difference that can be assigned to the words being that "matter" is used when all the properties of matter are taken into consideration, while "energy" is used when only its

dynamical properties are considered. The working out of the hypothesis is somewhat involved, and the author's views do not appear to lend themselves readily to satisfactory explanation within the limits of a small pamphlet, while the introduction of brief allusions to such subjects as Prof. Korn's work on telephotography merely complicates matters without really throwing any light upon the theory.

Studies in Plant and Organic Chemistry, and Literary Papers. By Helen Abbott Michael (Miss Abbott). With Biographical Sketch. Cambridge, Massachusetts: The Riverside Press. 1907.

It is perhaps unnecessary to emphasise the importance of Miss Abbott's work on Plant Chemistry, for most students of botany, physiology, and chemistry are familiar with her systematic studies of the analysis of plants and of the relations of chemical composition to plant species. In this volume are collected for the first time her scientific and literary papers, and they form a remarkable record of work done in a comparatively short life. The papers include reprints from the *Berichte der Deutschen Chemischen Gesellschaft* upon a new method of preparing aromatic nitriles, and on mandelic and crotonic acids, as well as various lectures upon different questions connected with plant chemistry. All her work shows a marked power of seeing all sides of a question, while the style of writing is straightforward and decisive; it must have required a sustained effort of steady application, such as is generally not supposed to be associated with brilliance of intellect, to carry her through the monotony of much of her work, and only a truly great investigator would have been unencumbered by the mass of detail she accumulated and have deduced the underlying generalisations.

When the reader turns to the biographical sketch the book contains he will find many surprises awaiting him. The characteristic features of Miss Abbott's work we have touched upon, and it is not a matter of difficulty to conjure up an outline of a personality by whom this work could have been produced, but the result will very probably be totally different from the true individual described in the biography. In place of a patient worker, wrapped up in scientific work, enduring and even plodding, we meet with a charmingly versatile woman, whose sympathies were unbounded and tastes catholic, in whom, among her manifold gifts, the one for scientific work seems almost incidental. Her early years were devoted to the study of music, in which authorities who were eminently qualified to judge considered she was destined to excel; however, in 1882, when 25 years of age, she entered on a course of medicine, which, partly owing to ill-health, she had in turn to relinquish for research work in plant chemistry. In this region she quickly won distinction in American scientific circles, and in 1887 she paid a lengthy visit to Europe. By this time her reputation had spread both in England and on the Continent, and in the course of the tour she made the personal acquaintance of many famous chemists. Her experiences are related frequently in her own words in the biograpical sketch, some notes which she jotted down from time to time, and afterwards copied into a book, having been drawn upon in order to give a view of her impressions of her pilgrimage. All her notes reveal a genuine enthusiasm, keen powers of observation, and abundant vitality, combined with a sense of humour. One particular pleasant feature is the mutual relations which seem in all cases to have existed between her and the many eminent men with whom she came in contact; always we see the same grateful and deferential recognition on the one side of the cordiality manifested on the other. Her philanthropic work, her artistic talent, and finally her literary ability are all characteristic features of her wonderful versatility, the literary papers showing that not only had she read widely, but had also assimilated what she had read and made it her own, while every subject she touched upon was illuminated by the originality of her thoughts and her critical powers of analysis.

The book is one which will appeal to many readers—students of science and literature will find that it contains much to interest them, lovers of biography will enjoy the brightly-told tale of a full and happy life, and to those who believe in the mental powers of women it will give a striking vindication of their beliefs, such as has not perhaps its equal in the history of the achievements of women in the intellectual world.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 22, June 3, 1907.

Selenium Hexafluoride.—Sir William Ramsay.—Lebeau (*Comptes Rendus*, cxliv., 1042) has suggested that the gaseous compound obtained by Prideaux is an oxyfluoride of selenium, giving as his reason for this suggestion that Prideaux relied upon the density of the gas and its physico-chemical relations with the hexafluorides of sulphur and tellurium. The author has himself determined the density of the gas, which he finds to be 97·23. If the formula were $SeOF_4$ the density would be 85·5, and if SeO_2F_2 it would be 74·5, and thus there appears no room for doubt that it is the compound SeF_6. Possibly in presence of a reducing agent, such as copper, selenium will not form a hexafluoride.

Preparation of a Continuous Current of Oxygen at Constant Pressure.—Gustave D. Hinrichs.—Oxygen may be conveniently prepared for lecture and analytical purposes in a Kipp, charged with large lumps of pyrolusite, which has been well washed to remove all particles of dust. The liquid employed is commercial oxygenated water acidulated with one-twelfth of its volume of concentrated sulphuric acid, which is added slowly, keeping the liquid at a low temperature. The generation of gas is as steady and regular as when hydrogen is evolved by the action of hydrochloric acid upon zinc. It is essential that the solid should be present in excess, and should nearly fill the middle bulb; also the pressure must be relieved when the gas is no longer required.

Action of Silicon Tetrachloride on Silver and Copper.—Em. Vigouroux.—When silver is subjected to the action of silicon tetrachloride at a high temperature, the metal becomes coated with a layer of silver chloride. If this is removed with ammonia, it is found that the loss of weight is 8·33 per cent. The ingot obtained contains no silicon, free or combined. When copper is used it is found that a compound of copper and silicon is obtained, which contains about 2·7 per cent of silicon, corresponding to $Cu_{16}Si$. The copper thus treated retains its malleability and its red colour, and is easily attacked by nitric acid, while other acids and alkaline liquids either have no action upon it or else attack it only very slightly.

Transformation of Ethereal Salts of α-Brominated Fatty Acids into Ethereal Salts of α-Iodated Fatty Acids.—F. Bodroux and F. Taboury.—Iodine reacts with magnesium in presence of a large excess of ethyl oxide, giving an ethereal solution of magnesium iodide. This reacts energetically with halogen ethers, and if the product of the reaction is treated with water, the ethereal layer decanted and shaken up with water, the iodated compound is obtained, the general reaction being—

$$2R{-}CHBr{-}COOC_2H_5 + MgI_2 = 2R{-}CHI{-}COOC_2H_5 + MgBr_2.$$

The yield is practically quantitative, and the authors have

prepared by this method ethyl iodo-acetate, ethyl α-iodo-propionate, ethyl α-iodo-butyrate from the corresponding bromine compounds. The iodine compounds decompose rapidly, setting free iodine under the influence of light and heat. At ordinary temperatures they emit very irritating vapours.

Dimethoxyheptane-1 . 7, $CH_3O(CH_2)_7.OCH_3$. — J. Hamonet. — The following reaction occurs when a haloid methyl ether acts upon the magnesium derivative of a polymethylene haloid ether :— $RO(CH_2)_nMgX + XCH_2OR' = MgX_2 + RO(CH_2)_{n+1}OR'$; and this is a general method of passing from one homologue to the next above it. This method, however, is tedious when higher homologues are required, and it may be considerably shortened in the case of compounds containing an odd number of carbon atoms if a formic ether, HCO_2R, is substituted for the methylene haloid ether ; a di-ether of a symmetric glycerin is then obtained on addition of water, viz., $RO(CH_2)_nCHOH(CH_2)_nOR$. The di-ether alcohol when treated with phosphorus trichloride gives a chlorinated diether, $RO(CH_2)_nCHCl(CH_2)_nOR$, and if the chlorine is replaced by hydrogen, the compound $RO(CH_2)_{2n+1}OR$ containing $2n+1$ carbon atoms is obtained from the ether containing n carbon atoms. These transformations when applied to dimethylene heptane triol 1 . 4 . 7 and dimethoxychloroheptane, which can be hydrogenated by the action of sodium, give dimethoxy-heptane.

Synthesis of Auramines by Oxalic Ethers.—A. Guyot.—When oxalic ethers condense with tertiary aromatic amines the secondary products of the reaction give with acids an indigo blue aqueous solution of neutral salts. Dilute ammonia precipitates these aqueous solutions, giving not the corresponding hydrol but a tetramethyl-diamidodiphenyl amidoacetic ether according to the equation—

$$\begin{matrix} R_2N{-}C_6H_4 \\ R_2N{-}C_6H_4 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} Cl \\ CO_2R' \end{matrix} + 2NH_3 =$$

$$= NH_4Cl + \begin{matrix} R_2N{-}C_6H_4 \\ R_2N{-}C_6H_4 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} NH_2 \\ CO_2R' \end{matrix}.$$

These new substances have all the properties of the leucoauramines, giving a blue coloration with glacial acetic acid, and condensing with the tertiary aromatic amines, giving derivatives of triphenylmethane. Thus, when an equimolecular mixture of dimethyl aniline and ethyl tetramethyldiamidodiphenyl amidoacetate in acetic acid solution is heated for some minutes on a water-bath, ethyl hexamethyltriamidotriphenylacetate is formed quantitatively according to the equation—

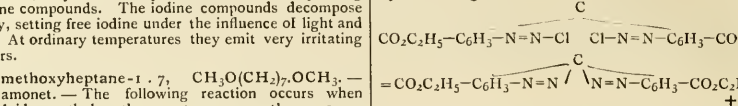
$$\begin{matrix} (CH_3)_2N{-}C_6H_4 \\ (CH_3)_2N{-}C_6H_4 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} NH_2 \\ CO_2C_2H_5 \end{matrix} + C_6H_5{-}N(CH_3)_2 =$$

$$= \begin{matrix} (CH_3)_2N{-}C_6H_4 \\ (CH_3)_2N{-}C_6H_4 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} C_6H_4{-}N(CH_3)_2 \\ CO_2{-}C_2H_5 \end{matrix} + NH_3.$$

To pass to the corresponding auramines a dilute solution of potassium ferricyanide can be used, when oxidation is instantaneous.

Action of Magnesium Organic Compounds upon Benzylidene Metamethylcyclohexanone.—Henri de Béville. — If ethyl magnesium iodide is allowed to act upon a concentrated ethereal solution of benzylidene metamethyl-cyclohexanone a thick liquid is obtained ; from it may be separated a crystalline product, the analysis of which shows that it is $C_{16}H_{22}O$. After rectifying the liquid product a colourless liquid is obtained, which appears to be $C_{16}H_{22}$. When propyl magnesium iodide is used the products of the reaction are $C_{17}H_{24}O$ and $C_{17}H_{24}$. In neither case can the hydrocarbon be obtained in a state of purity.

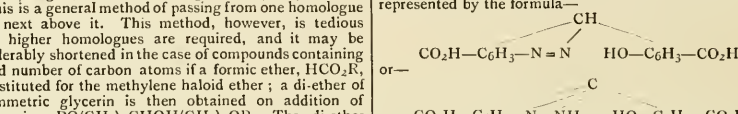
New Type of Diazo-compound. — H. Duval.— Diamidodiphenylmethanedicarbonate of ethyl is diazotised normally in a strongly acid solution at a low temperature, but when the temperature is raised, or when the liquid is not acid enough, a mixed diazo-compound is formed, the equation being—



$$CO_2C_2H_5{-}C_6H_3{-}N{=}N{-}Cl \quad Cl{-}N{=}N{-}C_6H_3{-}CO_2C_2H_5$$

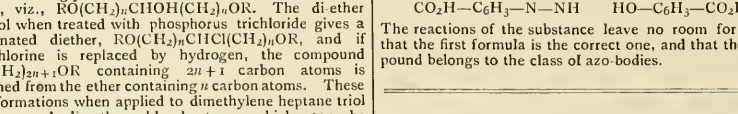
$$= CO_2C_2H_5{-}C_6H_3{-}N{=}N \quad N{=}N{-}C_6H_3{-}CO_2C_2H_5 + 2HCl.$$

Hot sulphuric acid acts upon the diazodiphenylmethane-dicarbonate of ethyl, giving a compound which may be represented by the formula—



$$CO_2H{-}C_6H_3{-}N{=}N \quad HO{-}C_6H_3{-}CO_2H,$$

or—



$$CO_2H{-}C_6H_3{-}N{-}NH \quad HO{-}C_6H_3{-}CO_2H.$$

The reactions of the substance leave no room for doubt that the first formula is the correct one, and that the compound belongs to the class of azo-bodies.

MISCELLANEOUS.

Prize for Life-Saving Apparatus for Use in Noxious Atmospheres.—The Council of the Society of Arts are prepared to award, under the Fothergill Trust, a Gold Medal, or a prize of £20, for the best portable apparatus or appliance for enabling men to undertake rescue work in mines or other places where the air is noxious. It is intended that the apparatus sent in shall be submitted to practical trials and tests. In the award of the Medal regard will be had, firstly, to excellence of design and contrivance, and, secondly, to excellence of manufacture. Credit will be given to such parts of the apparatus as are the invention of the exhibitor ; the object being to distinguish the apparatus which gives the best promise of being practically useful. Inventors intending to compete should send in a notice of their intention together with a full description of their inventions not later than March 31, 1908, to the Secretary of the Society of Arts, John Street, Adelphi, London, W.C., and in cases in which the apparatus has been put into actual use, the experience of such use should be given, and the special points of merit of the apparatus indicated. Notice of the place to which the apparatus is to be sent will be subsequently sent to those competitors whose apparatus the judges may desire to test, together with an indication of the tests, and of the manner in which they will be conducted. Competitors intending to patent their inventions should be careful to obtain protection, as the Council of the Society cannot undertake any responsibility as regards the secrecy of the whole, or of any part, of an invention submitted to them. The prize will be awarded on the report of judges appointed by the Council. The competition is not limited to British subjects. The Council reserve to themselves the right of withholding the prize, of extending the time for sending in, or of awarding a smaller prize or smaller prizes.—Henry Trueman Wood, Secretary.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Microbes in Soil.—Can any reader kindly point me to an authority for the remarkable statement which I have seen (but have tried in vain to recall where) that the organisms in soil where grass is grown are anaërobic, not aërobic, as in the case of other plants.—Quest.

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VOLUME XCVI.

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THE ESTIMATION OF CHROMIUM IN ALLOYS.

By ARCHIBALD ALLISON.

THE usual spur to investigation, an anxiety for certitude in his results, led the present writer to examine in detail methods of estimating chromium, particularly in alloys for steel-making purposes.

The two methods most widely employed are the sodium peroxide fusion and the tribasic dry oxidation.

The first was the one in use in this laboratory, and, somewhat modified, has, in the writer's hands, given the best results.

First of all, in this method, the alloy need not be particularly finely ground, as is commonly insisted. The writer grinds till the powder just begins to cling to the agate.

Secondly, the weight taken for each estimation is always 1 grm., as this relatively large weight has been found to make for greater accuracy.

The method is briefly:—

One grm. is fused in a nickel crucible with 8 grms. sodium peroxide. The melt is extracted with about ½ litre hot water, the liquid boiled for ten minutes to expel hydrogen peroxide, and filtered. The precipitate is fused again, as before; the extraction boiled and filtered and the precipitate washed. The mixed filtrates are acidified with sulphuric acid and titrated with ferrous ammonium sulphate and potassium dichromate.

The doubtful points were:—

1. Does the filter-paper reduce the chromic acid in the hot alkaline solution?
2. Does the oxide of nickel affect the subsequent titration?
3. Is a second fusion necessary?

With these points in view, estimations were carried through side by side with varying conditions.

It was noticed that, on filtering the second extraction through paper, the first portion of the filtrate was much more yellow in colour than the whole filtrate subsequently appeared, the conclusion being that this colour was caused by the first portion of the hot alkaline liquid attacking the paper. (This must occur with the first filtration also, the actual reduction of chromic acid probably taking place on acidifying). On filtering through asbestos this phenomenon is not apparent.

In some experiments the two filtrates were mixed, acidified with sulphuric acid, and boiled with the addition of a little potassium permanganate. The liquid was then diluted to about two litres, the permanganate destroyed with 60 or 70 cc. hydrochloric acid, and boiling continued till the liquid was quite free from chlorine. The results quoted are in all cases typical.

No. of alloy.	Treatment.	Cr obtained (per cent).
1.	*a.* Filtered extractions through paper ..	62·86
	b. Filtered extractions through asbestos	62·99
2.	*a.* Filtered extractions through paper ..	63·73
	b. Filtered extractions through paper and oxidised with $KMnO_4$	63·88
3.	*a.* Filtered extractions through paper ..	62·47
	b. Filtered extractions through paper and oxidised	62·61
5.	*a.* Filtered extractions through asbestos	61·54
	b. Filtered extractions through paper and oxidised	61·54

It is thus clear that filtering through paper causes low results, which can be avoided by subsequent oxidation or filtration through asbestos.

The next experiments were carried out in the presence of the nickel.

No. of alloy.	Treatment.	Cr obtained (per cent).
6.	*a.* Fused once; boiled extraction, cooled, acidified, and titrated. The black peroxide of nickel did not completely dissolve; end-point uncertain	65·01
	b. Fused twice and filtered through asbestos	62·19
	c. Fused twice, filtered through asbestos, and oxidised with $KMnO_4$	62·12
9.	*a.* Fused once; boiled extraction, acidified, and oxidised with $KMnO_4$; end-point obscured	62·14
	b. Fused twice; filtered through asbestos	62·16

In the case of alloy No. 6*a*, the black precipitate of nickel sesquioxide obviously oxidised the ferrous sulphate to give a false result.

In the case of No. 9, the boiling dissolved up the nickel sesquioxide and prevented its oxidising effect, but, as in No. 6*a* also, the end-point was obscured by the nickel in solution combining with the ferricyanide indicator. It is therefore highly desirable to filter off the nickel precipitate.

The third point was disposed of as follows:—

No. of alloy.	Treatment.	Cr obtained (per cent).
10.	*a.* Fused once; filtered through asbestos, boiled precipitate with water containing sodium peroxide and carbonate, and filtered again.	64·34
	b. Fused twice; filtered through asbestos each time	64·37

It is thus seen that a second fusion is not strictly necessary, but most chemists would doubtless regard it as advisable.

With reference to the tribasic dry oxidation method, the writer has obtained satisfactory results, but finds a liability for a portion of the alloy to adhere to the platinum dish very obstinately and cause low results.

Notes.—The writer takes as his standard re-crystallised potassium dichromate. The ferrous ammonium sulphate is added in the solid form. The very pure salt is re-crystallised rapidly to obtain pure small crystals, or ground to a coarse powder. This is then mixed in a large bottle and is standardised against the dichromate, portions being weighed out as required for each estimation.

The Laboratory,
Cammell, Laird, and Co., Ltd.,
Grimesthorp Steel Dept., Sheffield.

ON THE SEPARATION AND ESTIMATION OF SMALL AMOUNTS OF MANGANESE IN NATURAL SILICATES.

By PHILIP HOLLAND.

EACH year it may almost be said witnesses the birth of some process for estimating small quantities of manganese, such as are found to occur in the ashes of plants in mineral waters and in natural silicates.

Possibly the earliest of these minimetric schemes is that of Walter Crum by the lead peroxide process, and the latest that of Tarugi, who has recently observed that manganous hydroxide dissolves in glycerol and in course of its conversion to the higher oxide imparts to that solvent a ruby colour. This red colour can be made the basis of a colorimetric scheme for manganese.

It is now some eighteen years since I first began to analyse specimens of rock in order to furnish information to some of my friends who required it. In the interval many specimens have passed through my hands, and ever and anon I have felt a bit in doubt of the figure about to be recorded for the manganous oxide. Sparingly present in igneous rocks, it seemed likely that in the analytical separation some little might escape collection where it should be collected and turn up where it should not, viz., in the lime and magnesia precipitates. Manganese did at times turn up in these precipitates, and was determined colorimetrically by Crum's process, thus enabling the necessary corrections to be made.

It was the discovery of traces of manganese in the magnesian phosphate precipitate which suggested the experiments that form the subject of this article.

The sodium acetate process with double precipitation of the alumina and ferric hydroxide has always been the one employed to separate the manganese in the first instance. The further operations on the filtrate, its concentration and treatment with NH_4OH and H_2S, need no description.

The MnS precipitate requires several operations before the analyst can weigh his Mn_3O_4, for the sulphide has first to be converted to chloride, then to carbonate, and, lastly, to the oxide, which may fall short of the correct figure from loss, or be in excess of it owing to contained salts.

Seeking to abridge the process I have used the well-known reaction between manganic hydroxide and potassium iodide in the presence of slight excess of diluted chlorine-free hydrochloric acid.

The following solutions were prepared :—

1. A solution of manganous sulphate slightly acid, of which 5 cc. equalled 0·001 grm. of MnO.
2. A 10 per cent solution of pure NaOH.
3. A 5 per cent solution of pure KI.
4. Diluted HCl, equal volumes of acid and water.
5. A highly dilute solution of sodium thiosulphate.

The thiosulphate was standardised as follows :—Into a capacious flask was put 100 cc. of No. 1, and to it was added a slight excess of No. 2. The flask was then well shaken until the conversion of the manganous into manganic hydroxide was judged to be complete. Five cc. of No. 3 was next added, followed by as much of No. 4 as more than dissolved the hydroxide and rendered the solution clear of suspended particles. The contents of the flask after dilution with 150 cc. of water were then titrated with thiosulphate. This latter was so adjusted that 1 cc. equalled 0·0005 grm. of MnO under the recited experimental conditions. The thiosulphate does not for long retain its strength, but the fact is immaterial, for the operator has always at hand his manganous sulphate with which to check it. The scheme for separating the manganese from a solution, first as sulphide, and for finally estimating it indirectly as above, was tested as follows :—

Into a series of flasks was put a known amount of No. 1 along with 4 grms. of iron-free and otherwise pure NH_4Cl and 150 cc. of water at 60° C. The solutions were made ammoniacal, then saturated with H_2S, and the flasks closed and set aside for twenty-four hours. The MnS in each case was collected on a filter, and gently washed with a 5 per cent NH_4Cl solution containing a little $(NH_4)_2S$. What MnS adhered to the flask (it seldom did so) was removed by pure paper pulp, and the whole got on the filter. The wet filter next, cautiously folded, was dried and ignited in a 2½ inch Berlin crucible.

To the residue was now added ten drops of strong HCl, and the crucible gently rotated over a small flame till all oxide dissolved and Cl was quite away.

The resulting manganous chloride was put in the flask and dealt with just as for the standardising of the thiosulphate.

The following are trial experiments given in the order in which they were made.

One cc. of sodium thiosulphate equals 0·0005 grm. of MnO.

MnO taken. Mgrms.	Thiosulphate required. Cc.	MnO found. Mgrms.
10	20·1	10·05
10	19·7	9·85
5	9·6	4·80
5	9·5	4·75
5	9·8	4·90
2	3·8	1·90
2	3·6	1·80
2	4·2	2·10
2	3·4	1·70

I am disposed to attribute the slight loss which occurs to passage of MnS through the filter, or it may be that twenty-four hours' digestion with $(NH_4)_2S$ is insufficient to ensure complete precipitation of the sulphide. The scheme was now applied to the estimation of MnO in a solution made so as to simulate the filtrate from 1 grm. of some sedimentary rock after usual treatment and removal of SiO_2.

To this end I prepared a solution of the following oxides; 250 cc. of the solution represented 1 grm. of rock :

Al_2O_3	0·200
Fe_2O_3	0·080
MnO	0·002
CaO	0·009
MgO	0·024

The supposed rock would thus contain 0·2 per cent of MnO, an amount often met with in slates and shales from various geological horizons.

Taking 250 cc. of the solution, the $Al_2O_3+Fe_2O_3$ were thrown out by acetate. The precipitate was then filtered off and washed, and re-dissolved in excess of HCl, from which it was twice thrown down by NH_4HO. The united filtrate, after concentration and complete removal of any iron it might contain, was next dealt with in the manner just described.

Thiosulphate required.	MnO found.
Cc.	Per cent.
3·5	0·175
3·7	0·185
3·4	0·170
3·9	0·195
Average..	0·181

So far the analyst is assumed to be working in the entire absence of Cu, Ni, Co, Zn. Should these be present he would not straightway ignite his sulphide precipitate, but would modify his operations accordingly.

In the lime and magnesia precipitates from the sulphide filtrates I could detect at times a trace of manganese. Did it pass the filter when washing the MnS in spite of all precaution?

What has been said applies to the finding of manganese in non-metalliferous rocks and in such sedimentary material as they give rise to. For those analysts whose work lies in other grooves, who perchance may be attached to a steel-works and have to determine the manganese in several specimens of steel a day, the scheme I have set forth is, in respect of time required, quite out of the question. Most steel analysts I believe treat the steel in the first instance with HNO_3, and by means of some further oxidant get their manganese in a suitable condition for titration.

Within the past three weeks I have experimented on the reaction for manganese described by Dr. Hugh Marshall in 1901 (CHEMICAL NEWS, vol. lxxxiii., p. 76). This is the now well-known persulphate reaction, whereby ammonium persulphate reacting on manganous sulphate in the presence of silver nitrate and excess of nitric acid yields permanganic acid. Marshall, discussing the reaction and its sensitiveness, suggests that a colorimetric estimation of manganese could apparently be founded upon it.

This is so, for working on the lines suggested by Dr. Marshall I have succeeded in estimating quite easily the Mn in a specimen of iron wire and in two specimens of steel. When the Mn does not exceed 1 per cent the colorimetric determination can quite well be made on half a grm. of steel. The solutions should be well diluted to, say, 500 cc. after the reaction and development of the pink colour. The $KMnO_4$ solution, wherewith to match the colour in the reaction flask, contained 0·0005 grm. of Mn per cc.

Mn per cent colorimetrically by persulphate reaction.			Mn per cent by scheme described in this article.
Iron wire.	File steel.	Steel ring.	The same iron wire.
0·92	0·37	0·87	0·92
0·89	0·35	0·91	0·95
0·91	0·32	—	0·90
0·94	—	—	0·91

The matching of dark tints in flasks when the solution, owing to its deep shade, has to measure 500 cc. is much assisted towards the close by employing two small Nessler cylinders of the same bore. In one is put 10 cc. of the solution required to be matched, and into the other 10 cc. from the matching flask. Should the tints not correspond the contents of the second cylinder are returned to the matching flask, to which a further addition of the colouring reagent is made and the operation repeated. Probably most analysts who have not some form of tintometer work so, and thus soon arrive at correct adjustment for the tint required. It may perhaps be hardly necessary to say that the volume of liquid in the flasks must be alike, also that the matching flask must also contain some of the oxidising reagents.

The development of the colour reaction between the manganous salt and the reagents should be made in a small volume of solution. The operator with a little practice soon hits on the right conduct of the process, so that the colour shall develop, gradually assume its full shade, and not be obscured by suspended silver peroxide.

London, June 25, 1907.

CHEMICAL REACTION BETWEEN SALTS IN THE SOLID STATE.*

By EDGAR PHILIP PERMAN.

IT has long been known that in a mixture of solid salts chemical reaction may take place. Experiments on the subject have been made by Spring (*vide infra*), Thorpe (*B. A. Report*, 1881, p. 580), and others. My attention was first called to the question by observing that a mixture of arsenious oxide and cadmium nitrate underwent a slow but complete change of composition, the final result being that the nitric acid was eliminated, arsenic acid taking its place.

Preliminary Experiments.—Some experiments were made in order to discover what salts would be suitable for a careful investigation. The following were selected for trial, since a chemical change could be traced by an accompanying change of colour. The salts were finely powdered but not specially dried.

Salts.	Result on mixing.
Lead nitrate and potassium iodide	Immediate action.
Lead chloride and potassium iodide	Immediate action.
Lead formate and potassium iodide	Slow action.
Lead sulphate and potassium iodide	Very slow action, colour appearing after 30 mins.
Lead oxide (litharge) and potassium iodide	No appreciable action.
Lead carbonate and potassium iodide	No change.
Mercuric chloride and potassium iodide	Immediate action.
Mercuric cyanide and potassium iodide	No action.
Mercuric chloride and potassium chromate	Slow change.

From these salts two pairs were chosen for further study, viz., lead chloride and potassium iodide, and mercuric chloride and potassium iodide.

The salts were purified by re-crystallisation, dried over sulphuric acid, ground in a mortar, and sifted through fine silk cloth, such as is used for sifting flour; they were then kept in desiccators over sulphuric acid.

Lead Chloride and Potassium Iodide.

Effect of Drying over Sulphuric Acid.—Equivalent quantities of the salts (2 grms. potassium iodide and 1·68 grms. lead chloride) were placed in two flasks, A and B (Fig. 1), C containing concentrated sulphuric acid. The salts were occasionally warmed and shaken in order to make the drying more efficient. After standing forty-eight hours, the lead chloride was shaken from A into B, C being held in a horizontal position. The salts were mixed by shaking, when there was no apparent change of colour. The flask B, which had previously been drawn out, was then sealed off.

The mixture was watched from day to day; no change could be seen until the tenth day after mixing, when a very faint yellow colour appeared. On further keeping, the colour slowly deepened for some weeks, and then seemed to remain unaltered. In this experiment the mixture was kept in the dark.

Effect of Light.—Another mixture made in the same way, but exposed to daylight behaved in no way differently from the first.

Effect of Temperature.—On heating a similar mixture at 100° for five hours, no colour appeared, but on keeping it showed a tinge of yellow at the beginning of the third day, showing that the reaction had been much accelerated.

* A Paper read before the Royal Society, May 23rd, 1907.

Attempt to Determine the Minimum Quantity of Water necessary to Produce an Immediate Visible Reaction.

Several methods were tried:—

1. The mixture having been made in the usual way, the flask containing it was weighed, and allowed to stand open to the air on the balance pan until the yellow colour was perceptible. The increase in weight was then noted.

2. The flask containing the mixture was connected, by a ground glass joint and wide stopcock, with a small bulb containing crystallised borax. As soon as the yellow colour appeared, the bulb was detached, and the loss in weight of the borax determined.

3. The substances were dried over phosphorus pentoxide, and mixed in an exhausted globe. Measured volumes of air saturated with water vapour were then admitted until the first appearance of colour. The weight of water admitted was calculated.

The results obtained by these three methods were not very concordant, the quantity of water varying from 0·1 mgrm. to 1 mgrm. The smallest number is probably the most correct. The chief interest of the matter is in its comparison with the case of mercuric chloride and potassium iodide.

tube and contents were dried in the same way as the potassium iodide. The tube was then sealed off, and the salts were mixed by breaking the bulb.

As the result of these experiments, it was found that on mixing the salts a faint colour usually appeared at once. It was at first yellow, and changed slowly or quickly, according to the thoroughness of the drying, into the scarlet mercuric iodide. If the phosphorus pentoxide (in the pump) was of poor quality or had been much used, the red colour appeared immediately on mixing the salts, but otherwise three days were required for the full development of the colour.

With specially made phosphorus pentoxide, more complete drying was obtained, and there was no reaction. The arrangement used is shown in Fig. 2; A is the alloy septum. After introducing the salts B, B′, the tube was narrowed at C, C′. The phosphorus pentoxide was then placed at D D′, and the tube sealed off at both ends. Next, the phosphorus pentoxide bulbs were broken, and the whole allowed to stand for a month. The tube was then sealed off at C, C′, the alloy was melted and run into E, and the salts were mixed. No colour appeared, and after keeping three years still no change had taken place; the

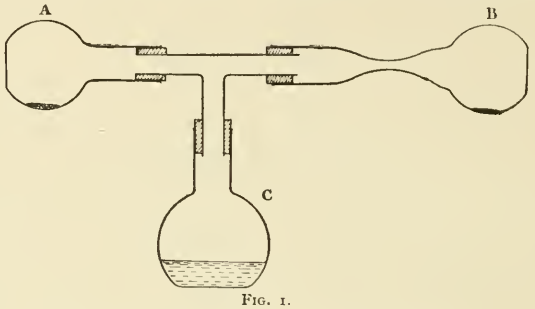


FIG. 1.

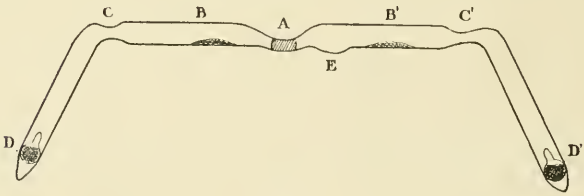


FIG. 2.

Mercuric Chloride and Potassium Iodide.

Owing to the volatility of mercuric chloride it was necessary to dry the salts separately, for otherwise some of the mercuric salt was driven over into contact with the potassium iodide. Several arrangements were used; in one a wide tube was divided by a glass septum, which was broken, after the salts were dried, by a glass rod enclosed. In another arrangement the separation was effected by a septum of fusible alloy, which was melted before mixing the salts.

The simplest device, however, was the following:—Some potassium iodide was placed in a small thin-walled bulb, and dried by gentle heating and at the same time exhausting with a mercury pump. The bulb was placed inside a wide tube closed at one end, and containing some mercuric chloride; the other end was drawn out, and the tube was then opened, when the red colour appeared. The contents of another tube, which had been kept the same time, and had accidentally contained some mercury, turned black on exposure to the air. No doubt the mercuric chloride (before drying) had been converted into a mercurous salt. The colour was the same as obtained on adding excess of potassium iodide solution to a solution of a mercurous salt.

Speed of the Reaction.—It is seen from these experiments that the reaction between mercuric chloride and potassium iodide takes place at an enormously greater rate than that between lead chloride and potassium iodide in the same conditions. The cause of the difference is at first sight not clear. The possible factors which may influence the rate of the reaction are:—(1) Quantity of water present; (2) solubility; (3) volatility; (4) degree of ionisation when

in solution. It is not necessary to consider the state of sub-division as the salts were all prepared in the same way. Solubility appears to be an important factor, for, on referring to the list of salts at the beginning of this paper, it is seen that the least soluble salts show the least action. Mercuric chloride is roughly ten times as soluble as lead chloride, but this would not account for the very great difference in the speed of the two reactions. The degree of ionisation of mercuric chloride in solution is extremely small, and this would have the opposite effect to that actually found. The volatility still remains to be considered; it is, undoubtedly, the determining factor, as shown by the following experiments:—In a wide tube constricted in the middle were placed, on one side some mercuric chloride, and on the other side potassium iodide. The tube was then sealed off, and watched from day to day. After the lapse of a month the margin of the potassium iodide was slightly coloured, and after three years the colour had travelled about 1 inch along the potassium iodide. The mercuric chloride remained free from colour. A similar experiment with lead chloride and potassium iodide showed no colour whatever. The difference was still more marked in another experiment in which the tubes were exhausted to 0·1 mm. The mercuric chloride coloured the potassium iodide *at once*, whilst after a year the lead chloride had had no effect.

Sodium Carbonate and Barium Sulphate.

In order to investigate the effect of a high temperature on reactions between solid salts, it was necessary to select those that were non-volatile. Sodium carbonate and barium sulphate were chosen; they have the further advantage that the extent of the reaction may be measured by extracting the mixture with water and estimating the sodium carbonate volumetrically.

Preliminary experiments were made in order to discover if any reaction took place during the process of extraction, and it was found that, if carried out quickly, there was no appreciable change. The following numbers were obtained:—

Na_2CO_3 taken.	$BaSO_4$ taken.	Treatment.	Na_2CO_3 found.
Grm.	Grm.		Grm.
0·454	1	Shaken with water 10 mins.	0·454
0·454	1	Allowed to stand with water 24 hours.	0·443

Effect of Heating.

Na_2CO_3 taken.	$BaSO_4$ taken.	Heated.	Temp.	Na_2CO_3 found.
Grm.	Grm.	Hours.		Grm.
0·841	1·045	5	300—400°	0·820
0·705	0·8035	35	,,	0·657

Although the temperature was considerably below the fusing-point of either salt, a marked reaction was thus found to take place. The heating was effected in a crucible without any precautions as to drying.

A mixture was then made of equivalent quantities of sodium carbonate and barium sulphate; it was ground lightly in a mortar for ten minutes, and dried over sulphuric acid. It was placed in a glass bulb at the end of a long tube, and heated in the vapour of bromnaphthalene (about 280°). The following are the results:—

Heated.	Na_2CO_3 originally present.	Na_2CO_3 found.
Hours.	Grm.	Grm.
35	0·2137	0·2155
54	0·5800	0·5831

At this temperature there is no sign of any decomposition.

The temperature of boiling sulphur (444°) was next tried. A mixture was used of two molecules Na_2CO_3 to one molecule $BaSO_4$.

	Heated.	Na_2CO_3 originally present.	Na_2CO_3 found.	Na_2CO_3 converted.
	Hours.	Grm.	Grm.	Per cent.
Series I.	20	0·5703	0·5355	6·10
	40	0·3671	0·3177	13·46
	65	0·4838	0·3971	17·92
Series II.	10	1·0224	0·9264	9·58
	16	0·8738	0·8057	7·79
	20	0·8655	0·7813	9·73
	40	0·4993	0·4581	8·25
	65	0·4970	0·4581	7·83

In the second series the mixture was somewhat drier than in the first, and the reaction appears to have ceased after a short time. The results are not very concordant, probably owing to irregularity in the quantity of moisture present.

In another series, a mixture of sodium carbonate and barium sulphate in molecular proportions was used. The salts were heated and allowed to stand over sulphuric acid before mixing. The mixture was then put into bulb tubes previously dried by exhausting with a water air-pump, and heating at the same time. The tubes were sealed, and heated in sulphur vapour.

	Heated.	$NaCO_3$ converted.	Na_2CO_3 left (calculated on total weight of mixture).
	Hours.	Per cent.	Per cent.
Series III.	10	10·92	27·84
	30	10·19	28·07
	60	11·60	27·62

Next a mixture was made of sodium sulphate and barium carbonate in molecular proportions, and was heated in sulphur vapour in order to discover whether the composition would become finally the same as in the last experiment:—

Heated.	$NaCO_3$ formed (on total weight of mixture).
Hours.	Per cent.
10	2·89
30	3·04
60	3·11

It would appear that the reaction in this direction is very much slower than in the other, and that equilibrium had not been reached; but it is impossible to say whether the two pairs of salts were in exactly the same condition with regard to moisture or not. Probably equilibrium had not been reached in either case.

Effect of Heat on a Mixture of Sodium Carbonate and Barium Sulphate in the absence of Moisture.

The substances were placed separately in a glass tube, and dried by heating and exhausting with a mercury pump. The salts were then mixed and heated fourteen hours in sulphur vapour. The result was—Sodium carbonate taken, 0·3071 grm.; found, 0·3074 grm. Thus no action takes place in the absence of moisture.

Effect of Shaking.—A mixture of 0·593 grm. sodium carbonate and 1·419 grm. barium sulphate was shaken in a closed flask for ten hours continuously. It was then found that 0·584 grm. sodium carbonate remained.

Effect of Percussion.—About 2 grms. of a mixture of two molecules Na_2CO_3 to one molecule $BaSO_4$ was placed in a heavy steel mortar with a closely fitting plunger as pestle. The latter was then hammered vigorously for thirty minutes, receiving about 900 strokes in all. On extracting with water, it was found that 4·87 per cent of the sodium carbonate had been converted into sulphate.

Effect of Pressure.—W. Spring (*Bull. Soc. Chim.*, xlvi., 160; xliv., 299) investigated reactions between sodium carbonate and barium sulphate, and between sodium sulphate and barium carbonate, under high pressures, and found that the extent of the reaction depended on the number of compressions and the time during which the mixture was left after compression.

These results were confirmed by the following experi-

ments:—A mixture of two molecules Na_2CO_3 to one molecule $BaSO_4$ was subjected in the steel mortar to a pressure of 82 tons (equivalent to 104 tons per square inch). It was then found that 1 per cent of the sodium carbonate had been converted into sulphate. It should be noted, however, that the mortar broke, so that the duration of the pressure was very short. In another experiment the pressure was 44·4 tons (56 tons per square inch, or about 8000 atmospheres), and its duration was one minute. The compressed mixture was then allowed to stand five weeks, when it was found that 4·02 per cent of the carbonate had been converted. Spring found that, after the mixture had been subjected to a pressure of 6000 atmospheres, and then left a month, 3·84 per cent barium sulphate had been converted into carbonate. It was found by Spring that mixtures of approximately the same composition were obtained, whether starting with barium sulphate and sodium carbonate or sodium sulphate and barium carbonate, thus showing that equilibrium had been attained. I have therefore confined myself to endeavouring to discover the effect of pressure on very thoroughly dried salts. The heavy mortar was first used. In order to dry the mixture, a hole was drilled sideways into the bottom of the mortar, and into this was cemented a tube containing phosphorus pentoxide. Molten wax was poured over the top of the plunger. However, the phosphorus pentoxide did not remain dry, and the result was that after the mixture had stood twenty-three days, and then been subjected to a pressure of 40 tons (equivalent to 51 tons per square inch, or 7600 atmospheres), 1·6 per cent of the sodium carbonate had been converted into sulphate.

In the next experiment the plunger passed through a rubber cork which fitted into the mouth of the mortar, and air and moisture were pumped out through the side tube. The drying was not complete owing to a slight leak and to the impossibility of shaking the powder. The result showed that 0·5 per cent of the sodium carbonate had been converted into sulphate by a pressure of 40 tons.

Owing to the difficulty of drying the salts in the heavy mortar, a lighter one was made in which the salts could be hammered, the blow of a hammer being essentially the same as a high pressure exerted for a very short time.

Effect of Percussion on thoroughly Dried Salts.—A steel mortar was made of 1⅛-inch internal diameter, with a loosely-fitting piston, and the piston rod passed through a rubber cork fitting tightly into the mouth of the cylinder. Several grms. of the mixture were placed at the bottom of the cylinder, and were dried by gentle heating and shaking, and at the same time exhausting the cylinder with a Fleuss pump. The piston was then hammered vigorously for thirty minutes (about 900 strokes). On analysing the mixture it was found that only 0·1 per cent of the sodium carbonate had reacted, an amount within the limits of experimental error. An exactly similar experiment was then made without specially drying the mixture; the salts had been dried over sulphuric acid, then mixed and kept in a well-stoppered bottle. In this case 2·38 per cent of sodium carbonate was converted into sulphate. The amount converted when the heavy mortar was used (*vide supra*) was 4·87 per cent. The areas of the pistons in the two cases were approximately as 1 : 2, *i.e.*, roughly the same as the extent of the reaction.

Influence of other Solvents.

Methyl Alcohol Vapour.—Lead chloride and potassium iodide were dried separately over phosphorus pentoxide, then mixed in a special apparatus, and exposed to the action of methyl alcohol vapour, the liquid having been carefully dried by quicklime. The mixture acquired a strong yellow colour in about one hour.

Benzene Vapour.—When exposed to benzene vapour in a similar way, no change took place.

A similar experiment with mercuric chloride and potassium iodide gave a similar result, except that the mixture gradually turned black owing to the reducing action of the metallic sodium left in the tube to dry the benzene.

Chloroform Vapour.—Some lead chloride was placed at the closed end of a wide glass tube. Inside the tube two sealed thin-walled tubes were placed, one containing potassium iodide and the other pure chloroform, each previously dried by phosphorus pentoxide. The wide tube was then exhausted by the mercury pump, and sealed off. On breaking the inner tubes, there was no apparent change of colour, either when the mixture was exposed to the action of the vapour or to that of the liquid. After standing a week a faint colour appeared. (Commercial phosphorus pentoxide was used in this experiment, so that the drying was not very perfect).

Ammonia.—Some ammonia gas was dried over lime, and allowed to stand with phosphorus pentoxide (Kahlbaum's) in a glass bulb. The bulb was then sealed off, and placed, together with a small bulb containing dry potassium iodide, in a wide tube containing lead chloride. The wide tube was then heated, exhausted, and sealed off. On breaking the inner tubes, no change was observed, and after keeping for a year it was still unaltered.

With regard to the action of these solvents, methyl alcohol dissolves and ionises both salts, benzene and chloroform dissolve neither, whilst liquid ammonia dissolves and ionises potassium iodide, but forms an insoluble compound with lead chloride (*Am. Chem. Journ.*, 1898, xx., 820).

Summary and Conclusion.

1. Salts in the solid state usually undergo double decomposition when mixed (and not specially dried).

2. Reaction between solid salts is accelerated by (1) heat, (2) pressure (including percussion), (3) shaking (no doubt by bringing fresh surfaces into contact).

3. The solubility and volatility of the salts greatly influence the reaction-velocity.

4. In the complete absence of water or other ionising solvent (*i.e.*, a solvent which becomes a conductor of electricity owing to the presence of the salt), *no reaction takes place.*

It would appear from these results that reaction between solid salts is of essentially the same nature as that between salts in solution. The quantity of water required to bring about a reaction is extremely minute, but its action is probably to ionise the salts. I would suggest that the water present forms a film on the surface of the salts, and that in this film minute quantities of the salts dissolve and there react. On this assumption, heat would accelerate reaction by increasing the solubility of the salts, and also by increasing their volatility if they had an appreciable vapour pressure. Pressure would in general bring more salt into solution, but would act chiefly by bringing the surfaces of the solids into close contact. Volatility would assist the reaction by carrying the particles of the volatile salt into contact with the surface of the other salt.

In the latter part of this work I have received most valuable assistance from Mr. J. H. Davies, B.Sc., to whom I here wish to express my indebtedness. I wish also to thank Professor A. C. Elliott for the use of the testing machine in the engineering department of this college.

Mercurammonium Base.—H. Gaudechon.—The author has shown that the mercurammonium base, $(NHg_2)_2O.nH_2O$, is formed instantaneously when mercuric oxide acts on dissolved ammonia. Five hydrates have been described, but only the monohydrate, $(NHg_2)_2O + H_2O$, is stable at the ordinary temperature in dry air. The hydrate with four molecules of water is stable in an atmosphere saturated with water vapour at 15°, and that with five molecules of water can exist only in presence of liquid water. Water at 100° decomposes the base into mercuric oxide and ammonia, $(NHg_2)_2O + 3H_2O = 2NH_3 + 4HgO$, and the brown oxide thus separated differs in crystalline form from the yellow and red varieties already known.—*Comptes Rendus*, cxliv., No. 23.

A METHOD FOR THE QUALITATIVE SEPARATION AND DETECTION OF FERROCYANIDES, FERRICYANIDES, AND SULPHOCYANIDES.

By PHILIP E. BROWNING and HOWARD E. PALMER.

THE ordinary method for the detection of ferrocyanides, ferricyanides, and sulphocyanides by means of ferric and ferrous salts leaves little to be desired in point of delicacy when these substances are not present together. When mixtures are to be examined, however, the colours tend to mask one another, and various methods to obviate the difficulty have been suggested, such as the bleaching of the red ferric sulphocyanide by mercuric chloride in testing for ferrocyanide, and the distillation of sulphocyanic acid before testing for that acid. In testing for a ferrocyanide in the presence of a ferricyanide the formation of the deep blue colour with the ferric salt or ferrous salt has generally been considered of sufficient delicacy for all practical purposes.

The work to be described is the result of an attempt to effect a separation of these substances one from another as well as to accomplish their detection.

Potassium ferrocyanide has long been mentioned as a precipitant of the ferrocyanides of the rare earth elements, cerium, thorium, yttrium, zirconium, &c., while it is also known that ferricyanides of these elements are soluble. These facts suggested the use of a member of the above mentioned group as a precipitant of the ferrocyanogen ion, and selection was made of a soluble salt of thorium as perhaps the most satisfactory and available.

A solution of potassium ferrocyanide was made by dissolving 1 grm. of the salt in a litre of water, and measured portions of this solution were used when amounts of 5 mgrms. or less were required. This solution was neutral to litmus and remained so throughout the investigation, as shown by frequent tests.

The delicacy of the reaction was tested by adding to portions of the solution enough water to make the total volume between 5 cc. and 10 cc., acidifying faintly with acetic acid or hydrochloric acid and adding a few drops of a 10 per cent solution of thorium nitrate. Amounts of the ferrocyanide as small as 0·0001 grm. gave a distinct cloudiness to the solution. Similar experiments made in the presence of 0·1 grm. of potassium ferrocyanide and 0·1 grm. of potassium sulphocyanide showed that these salts did not interfere with the delicacy of the test. In order to test the effect of dilution and the highest delicacy of the reaction, some precipitations were made in 100 cc. and 500 cc. of water, and it was found possible to detect 0·0005 grm. in 100 cc. of water and 0·0010 grm. in 500 cc. of water, or one part of the ferrocyanide in 500,000 parts of water.

The presence of considerable amounts of alkali acetates have a tendency to decompose the thorium ferrocyanide into soluble products, but this tendency may be overcome by further addition of thorium salt or hydrochloric acid.

Some difficulty was found in filtering the thorium ferrocyanide on paper alone, on account of its finely divided condition, but this difficulty was removed by agitating the liquid and suspended precipitate with some finely shredded asbestos before filtration.

In making the choice of a precipitant for the ferricyanogen ion with a view to subsequent testing for the sulphocyanogen ion by the ferric salt, some reagent giving a colourless solution was preferable. Salts of the elements zinc and cadmium meet this condition, and cadmium salts proved to be the more delicate. Following the general method already mentioned, it was found that 0·0001 grm. of the fericyanide could be readily detected in from 5 cc. to 10 cc. of water acidified with acetic acid even when 0·1 grm of potassium sulphocyanide was present. The cadmium ferricyanide presented the same difficulty in filtration that has been described in the case of the thorium ferrocyanide, and the difficulty was overcome in the same manner.

The method as recommended is as follows:—The solution to be tested, preferably dilute and about 5 cc. to 10 cc. in volume, is acidified faintly with acetic acid or hydrochloric acid and treated with a soluble thorium salt to complete precipitation. To the liquid and suspended thorium ferrocyanide some finely shredded asbestos is added, the whole is agitated and thrown on a filter, and the precipitate washed with a little water.

The presence of the ferrocyanide may be confirmed by decomposing the washed precipitate with strong sodium hydroxide on the filter, acidifying the clear filtrate with hydrochloric acid, and testing with ferric chloride.

The filtrate from the thorium ferrocyanide is treated with a soluble cadmium salt to complete precipitation of the cadmium ferricyanide, which after the addition of the asbestos is filtered and washed as previously described. The presence of the ferricyanide may be confirmed by treating the cadmium ferricyanide with sodium or potassium hydroxide, acidifying the filtered solution, and testing with a ferrous salt.

The filtrate from the cadmium ferricyanide is acidified with hydrochloric acid and treated with ferric chloride, which gives the red ferric sulphocyanide.

The method is especially recommended for the detection of small amounts of ferrocyanides and ferricyanides in the presence of each other. The following table gives some results obtained:—

$K_4FeC_6N_6$ present. Grm.	$K_3FeC_6N_6$ present. Grm.	KSCN present. Grm.	Indication.
	Tests for $K_4FeC_6N_6$ *only*.		
0·0010	0·1	0·1	Distinct.
0·0005	0·1	0·1	
0·0002	0·1	0·1	
0·0001	0·1	0·1	
	Tests for $K_3FeC_6N_6$ *only*. (These tests were made without waiting to wash the ferrocyanide precipitate thoroughly).		
0·1	0·0010	0·1	Distinct.
0·1	0·0005	0·1	Fairly distinct.
0·1	0·0002	0·1	Faint.
0·1	0·0001	0·1	Very faint.
	Tests for KSCN *only*.		
0·1	0·1	0·0010	Distinct.
0·1	0·1	0·0005	
0·1	0·1	0·0002	
0·1	0·1	0·0001	
	Tests for $K_4FeC_6N_6$, $K_3FeC_6N_6$, *and* KSCN.		
0·0100	0·0100	0·0100	Good tests for $K_4FeC_6N_6$, $K_3FeC_6N_6$, and KSCN.
0·0050	0·0050	0·0050	
0·0010	0·0010	0·0010	
	Tests of Mixtures Unknown to Analyst.		
0·0010	0·0010	—	Found: $K_4FeC_6N_6$ and $K_3FeC_6N_6$.
0·0010	—	0·0010	Found: $K_4FeC_6N_6$ and KSCN.
0·0010	0·0010	0·0010	Found: $K_4FeC_6N_6$, $K_3FeC_6N_6$, and KSCN.

—*American Journal of Science*, [4], xxiii., No. 138.

His Majesty the King of Greece has conferred upon Mr. Geo. G. Blackwell the Gold Cross of Officer of the Royal Order of The Saviour, this decoration being made in recognition of his services in connection with the development of the mining industries of Greece. Mr. Geo. G. Blackwell is chairman of the firm of Geo. G. Blackwell, Sons, and Co., Ltd., of Liverpool and London.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1907.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Arthur John Banks, 61, Lawton Road, Waterloo, Liverpool; John Kaye, M.A., B.Sc., Westerfield, Perth; Marcus Wechsler, D.Sc., 136, Sinclair Road, Kensington, W.

Certificates have been authorised by the Council under By-Law I. (par. 3) in favour of Messrs. David Leo Behrmann, 75, Sivewright Avenue, Doomfontein, Transvaal; William Bush Schober, B.Sc., Ph.D., Lehigh Univ., South Bethlehem, U.S.A.

A Ballot for the Election of Fellows was held, and the following were subsequently declared duly elected:—William Arthur Colebourn; Hugh Hague Copping, B.A.; Matthewman Dalton Cowap; Owen Aubrey Elias; Eugen Fischer, Ph.D.; Walter George Gledhill, M.A.; John Atkinson Jennings; Charles William Lamb Jensen; Percival George Lloyd; Walter Harold Nuttall; Harold Pochin, B.A.; Ruchi Ram Sahni, M.A.; Charles Kenneth Tinkler, B.Sc.; Charles Horne Warner; Walter Ormston Young; Israel Hyman Zortman, B.Sc.

Of the following papers those marked * were read:—

* 134. "*Some Properties of Radium Emanation.*" By Alexander Thomas Cameron and Sir William Ramsay, K.C.B.

It has been discovered that the emanation from radium undergoes a rapid change of volume shortly after its change from the solid to the gaseous state; this is followed by a slow change, corresponding with its loss of electrical activity. Glass tubes, as well as silica tubes, were used for the experiments. The absorption of helium, hydrogen, oxygen, and carbon dioxide was investigated in these tubes so as to estimate the necessary corrections for the loss of volume by the emanation. It has been shown by thirty sets of measurements that the emanation behaves in accordance with Boyle's law, both before and after this preliminary change. Measurements have been made of the initial volume of the emanation, obtained from a solution of 87·7 mgrms. of radium (metal) as bromide and sulphate. From these it would appear that, instead of the previously accepted value for the average-life-period of radium, 1100 years, a much shorter life must be deduced, namely, 236 years. The change of fresh emanation is accompanied by a halving of its volume, and reasons were adduced for the belief that this change corresponds with its polymerisation from Em^1 into Em^2; the change, as shown by time measurements, is a unimolecular reaction, and the subsequent rate of contraction agrees numerically with the loss of electrical activity. It has also been shown that helium, contained in silica vessels, may pass into the walls, but the conditions under which this absorption takes place have not been elucidated. Lastly, a deposit consisting doubtless of radium D has been observed; it is a brown substance, with a submetallic lustre, not easily attacked by oxygen. The half-life-period of radium D is said to be forty years, whilst those of radium A, B, and C are only a few hours.

Discussion.

Professor Clowes asked whether statements made by Dr. Thorpe that afternoon, which were supplementary to his Bakerian lecture, might not explain the presence of free hydrogen after exploding the mixture of oxygen and hydrogen arising from the decomposition of water. The lecturer had mentioned that he had invariably noticed an odour of ozone and of hypochlorite from solutions of radium bromide. If ozone were formed, this would lead to removal of oxygen by the action of the mercury in the pump, and if hypochlorite were produced, oxygen would remain combined in the solution. An excess of hydrogen would in either case remain after the explosion.

Mr. Baly asked whether it were not possible that the discrepancy between Sir William Ramsay's and Prof. Rutherford's values for the life of the radium atom could be explained by the life being shortened in the presence of the emanation. It was necessary to assume that the radium atom was in a very unstable condition, and it appeared possible that its disintegration might be assisted by the bombardment due to the decomposition of the emanation. Prof. Rutherford made his observations with a very thin layer of radium bromide on a plate from which the emanation readily escaped. Sir William Ramsay on the other hand allowed the solution of radium bromide to stand for periods of four days during which time the emanation was concentrating in the solution.

In reply to a question from Prof. Rutherford, Sir W. Ramsay stated that the emanation, when it passes from the solid to the gaseous state, passes at once into a monatomic gas, although one would imagine that a diatomic gas would be preferably formed. This may conceivably be connected with another unusual phenomenon which it displays; for at 80° the diatomic gas reverts almost entirely to its monatomic state, at 132° the reversion is not so complete, and at 237° still less complete. This is contrary to the general behaviour of compounds, yet it is not inconceivable that a higher temperature might prove favourable to combination and that a diatomic gas may be more stable at high than at low temperatures. The author, however, maintained that he was there to chronicle and not to defend the behaviour of the emanation.

The volume of helium produced from 1 volume of an emanation is about 3½ volumes—agreeing in this respect with Prof. Rutherford's contention that the α-particle is a helium atom. In reply to Prof. Clowes, it was pointed out that no ozone is produced from a solution of radium bromide although the solid bromide has an odour of ozone.

*135. "*The Affinity Constants of Aminosulphonic Acids as Determined by the Aid of Methyl-orange.*" By Victor Herbert Veley.

In continuation of a former investigation on this subject (*Trans.*, 1907, xci., 153) the affinity constants of certain aminonaphtholsulphonic acids have been determined, and the general results are as follows:—

1. The affinity constants of the aminonaphtholsulphonic acids when determined by the tintometer method show, as regards the effect of the introduction of the hydroxyl grouping in the naphthylaminesulphonic acids, relationships similar to those observed by Ostwald by the electric conductivity method for the hydroxybenzoic acids as compared with benzoic acid.

2. One possible case of steric hindrance induced by the introduction of the hydroxyl grouping in the 8-position was noted.

Attempts were made to examine the naphtholsulphonic acids by the above method, but the acidic reaction appeared to be mollified by some subsequent secondary change.

*136. "*Azo-Derivatives of* 1 : 3-*Diphenylbarbituric Acid. Dynamic Isomerism among the Coloured Hydrazones of* 1 : 3-*Diphenylalloxan.*" By Martha Annie Whiteley.

In order to throw some light on the structure of the compounds obtained by the action of aromatic diazonium chlorides on the 5-alkyl-substituted derivatives of 1 : 3-diphenylbarbituric acid (*Proc.*, 1906, xxii., 201), the investigation has been extended, and the action of the β-substituted derivatives of phenylhydrazine on 5 : 5-dibromo-1 : 3-diphenylbarbituric acid has been examined. The results show that the compounds obtained in the first reaction are *azo*-derivatives, whilst those obtained in the second are *hydrazones*.

In the course of the investigation the following com-

pounds have been prepared :—5-*Benzeneazo*-5-*benzyl*-1 : 3-*diphenylbarbituric acid*,—

$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>C<\begin{matrix}CHPh\\N:NPh\end{matrix};$$

5-*benzeneazo*-5-*diphenylmethyl*-1 : 3-*diphenylbarbituric acid*,—

$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>C<\begin{matrix}CHPh_2\\N:NPh\end{matrix};$$

the *nitro*-derivative,—

$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>C<\begin{matrix}CHPh_2\\N:N\cdot C_6H_4\cdot NO_2'\end{matrix}$$

melt and decompose at 170—171°, 160°, and 175° respectively. These compounds are yellow. 1 : 3-*Diphenylalloxanphenylmethylhydrazone*,—

$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>C:N\cdot NPhMe;$$

1 : 3-*diphenylalloxandiphenylhydrazone*,—

$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>C:N\cdot NPh_2;$$

1 : 3-*diphenylalloxanphenylbenzylhydrazone*,—

$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>C:N\cdot NPh(CH_2Ph),$$

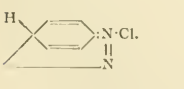
melt and decompose at 175°, 254—255°, and 130—131° respectively; these compounds exist in two forms, one yellow and one red.

"137. "*A Series of Coloured Diazo-salts derived from Benzoyl*-1 : 4-*Naphthylenediamine*." By Gilbert Thomas Morgan and William Ord Wootton.

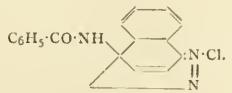
The examination of the diazo-salts of benzoyl-*p*-phenylenediamine and benzoyl-1 : 4-naphthylenediamine has been continued and it has been found that the diazo-derivatives of the latter base are extremely stable substances which are invariably coloured.

Benzoyl-4-*aminonaphthalene*-1-*diazonium chloride*, $C_6H_5\cdot CO\cdot NH\cdot C_{10}H_6\cdot N_2\cdot Cl$, m. p. 140° with decomposition, crystallises in well-defined yellow needles which retain their colour after repeated crystallisation from water or fractional precipitation from different organic media. The corresponding *bromide*, *iodide*, *sulphate*, *nitrate*, *nitrite*, *chlorate*, *perchlorate*, *carbonate*, *trichloracetate*, and *thiocyanate* have been prepared. The sulphate crystallises in golden-yellow leaflets or needles, whilst the perchlorate, which is quite stable in the dry state, separates in sparingly soluble, light yellow crystals, and is the palest compound of the series. These compounds have the chemical properties of diazonium salts, and couple readily with alkaline β-naphthol to furnish azo-derivatives. With potassium cyanide they yield *benzoyl*-4-*aminonaphthalene*-1-*diazocyanide*, a stable red microcrystalline compound which does not couple with alkaline β-naphthol.

These coloured salts might be regarded either as *syn*-diazo-derivatives or as equilibrium mixtures of diazonium and *syn*-diazo-derivatives, although their great stability somewhat militates against the assumption that they consist wholly or in part of *syn*-diazo-compounds. The existence of such a series of coloured diazo-salts would be anticipated from the formulation recently suggested by Cain for diazonium salts (Formula I.).



I.

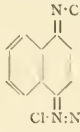


II.

According to this view, the appearance of colour in the foregoing series may be connected with the replacement of a benzene by a naphthalene nucleus and the substitution of the hydrogen atom of Formula I. by the heavy group $C_6H_5\cdot CO\cdot NH$ of Formula II.

Discussion.

Dr. Hewitt thought it very probable that coloured diazonium salts might possess a quinonoid structure. But as in all cases when the salts were coloured they allowed of a true quinonoid formulation, Dr. Morgan's compound might well have the constitution—



whilst the constitution Dr. Morgan assigned to the salt more resembled that of the "chinols" of Bamberger, which are colourless.

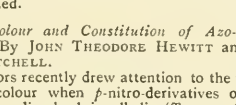
Dr. Cain thought there was much danger in speculating as to the colour of a compound entirely from the quinonoid or non-quinonoid state of only a part of the molecule. The rest of the molecule, as Dr. Morgan had pointed out, was of much importance in attempting to arrive at an explanation of the colour.

In reply, Dr. Morgan said that he preferred the formula for diazo-salts advocated by Dr. Cain to those which required the presence of a labile hydrogen atom in the para-position to the diazonium complex because the former configuration was applicable both to the simpler colourless diazonium salts and also to the more complex coloured diazo-derivatives described in this communication. The development of colour in this series of substances seemed to depend to some extent on the nature of the aromatic nucleus and partly on the presence of a complex substituent in the para-position to the diazo-nitrogen. Further experimental evidence, however, would be required before the conditions determining the appearance of colour among the diazonium derivatives could be completely defined.

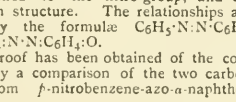
"138. "*Colour and Constitution of Azo-compounds*." (Part I.). By John Theodore Hewitt and Herbert Victor Mitchell.

The authors recently drew attention to the very marked change in colour when *p*-nitro-derivatives of arylazo-*p*-phenols were dissolved in alkalis (*Trans.*, 1896, lxxxix., 13, 17). The explanation was offered that whilst benzeneazophenol forms alkaline salts of corresponding constitution, the *p*-nitro-derivatives furnish salts with the metal attached to the nitro-group, and therefore diquinonoid in structure. The relationships are rendered apparent by the formulæ $C_6H_5\cdot N:N\cdot C_6H_4\cdot OK$ and $KO_2N:C_6H_4:N\cdot N:C_6H_4:O$.

Definite proof has been obtained of the correctness of this view by a comparison of the two carboxylic acids derived from *p*-nitrobenzene-azo-*a*-naphthol of the formulæ—



and—



Both these compounds give deep blue alkaline solutions, but, whilst the former yields brown precipitates with salts of heavy metals, the latter gives blue precipitates; no doubt in the latter case the lead salt has the constitution $O:C_{10}H_6:N\cdot N:C_6H_3<\begin{matrix}CO\cdot O\\NO\cdot O\end{matrix}>Pb$.

The following compounds were described :—

2-*Nitro*-5-*acetylaminobenzoic acid*, m. p. 210—220° (with decomposition). 2-*Nitro*-5-*aminobenzoic acid*, m. p. about 235°. p-*Nitro*-m-*carboxybenzeneazo*-α-*naphthol*, m. p. 260°. o-*Nitrobenzeneazo*-α-*hydroxy*-β-*naphthoic acid*, m. p. 200°. m-*Nitrobenzeneazo*-α-*hydroxy*-β-*naphthoic acid*, m. p. 220—225°. p-*Nitrobenzeneazo*-α-*hydroxy*-β-*naphthoic acid*, m. p. 242°. p-*Nitro*-m-*carboxybenzeneazophenol*, m. p. 195°. p-*Nitro*-m-*carboxybenzeneazo*-o-*nitrophenol*, m. p. 213°. p-*Nitro*-o-o-*dibromophenol*, m. p. 205—206°. p-*Nitrobenzeneazosalicylaldehyde*, m. p. 192—193°; its *acetyl* derivative, m. p. 150°, and *phenylhydrazone*, m. p. 235—240°. The melting-points in this and the preceding papers are uncorrected, the decomposition which occurs rendering accurate observation impossible.

The general result arrived at is that the frequency of the absorbed light is lowered by increase in the length of the chain of alternate single and double linkings. The introduction of substituents may modify the length of the chain owing to the possibility of more stable salt formation in other directions.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, June 14th, 1907.

Mr. H. M. ELDER, Vice-President, in the Chair.

A PAPER by Mr. UPSON, on the "*Electric Arc*," was read by the author.

It dealt with observations made during the past Session at the Pender Electrical Laboratory, at the suggestion and under the direction of Prof. Fleming, F.R.S., with the object of elucidating some of the facts connected with the production of electric arcs between cooled metal and carbon terminals, in air and hydrogen. Apparatus was exhibited for maintaining the arc in various gases, while one electrode was cooled by means of a water circulation. Arcs were described in which the electrodes consisted of carbon, copper, iron, and aluminium in different combinations, maintained in air, hydrogen, and coal-gas. With 110 volts supply, metal arcs in hydrogen took the form of a spark-discharge. At that voltage the maximum length of arc it was possible to obtain, with current up to 15 ampères, was 0·05", except where both electrodes were of the same metal. When carbon is one of the electrodes a true arc is formed. If carbon is negative the maximum length of arc with the above voltage is 0·07". Volt-ampère characteristic curves were shown for arcs in air and hydrogen of length 0·05". The general position of the curve is determined by the material of the negative electrode. With carbon negative, in hydrogen, the curves for various positive electrodes very nearly coincide. With carbon positive, they keep the same curvature, but vary in distance apart, according to the material of the negative. In general, the position of the curve is governed by the negative, but its particular shape seems to come from the influence of the surrounding gas. The slope of the curve (ampères horizontal, volts vertical) of the carbon arc in air, is much less steep than that of the curve of any arc in hydrogen. The former curve cuts the latter in the neighbourhood of 6·5 ampères. The curve for the arc with carbon positive, aluminium negative, in air, is very steep, being equal in this respect to the curves for arcs in hydrogen. Volt-ampère characteristics were shown for copper arcs in air, with (1) positive electrode cooled, (2) negative electrode cooled, and (3) neither cooled. Equations for various arcs were obtained giving the voltage in terms of current and arc-length. It was much more difficult to obtain a carbon arc in hydrogen with alternating currents; and no arc could be obtained when the electrodes were copper positive, and carbon negative, with 100 volts supply and frequencies of 50 and 80. Similar results were obtained in coal-gas. Apparatus was devised in accordance with a suggestion by Dr. Fleming, to interrupt the arc for a definite period of time. Experiments were tried to determine how long the arc could remain extinguished without losing the power of re-starting itself when the electromotive force was again applied. Curves were shown for arcs with electrodes of solid and cored carbons, in air. With cored carbons the time of interruption is greater than with solid, and both are much greater than that for the copper-carbon arc. In hydrogen the copper-carbon arc could not be made to re-start itself if the electro-motive force was removed for more than 0·04 of a second, and for this arc the minimum interruption possible is far shorter than for any carbon arc in air.

Mr. W. DUDDELL said the paper was a most interesting one. He asked it the author had noted the character of the different arcs which he had used. The characteristic curves for arcs in coal-gas or hydrogen were steeper than those in air, and therefore arcs in coal-gas were more suitable for the production of oscillations. He asked if the curves remained steep when the current was quickly changed. He had noticed the phenomenon of an arc between two cored carbons re-lighting, and said that on high-voltage circuits the length of time was considerable, and amounted in some cases to seconds.

Mrs. AYRTON said the paper was a valuable one, but she was sorry the author had not given a careful description of the appearance of the arcs and carbons under different conditions, and also the observations upon which the curves were founded. It was difficult to arrive at any general conclusions from the author's curves. The steep parts depend not only on the composition of the electrodes but on their size and on the length of the arc. The author had only used short arcs which with carbons only gave the flat part of the curve. With metal-carbon you get the steep part. Mrs. Ayrton also expressed her interest in the re-lighting experiments shown by the author.

Mr. A. CAMPBELL asked if the characteristic curve of a mercury arc was similar to that of the other metal arcs investigated. He pointed out that the use of unscientific units (inches and feet) in giving the results of such interesting researches was most deplorable. In all standard work on the subject the lengths of arc are always given in millimetres, and even in commerce the diameters of carbons are similarly expressed (*e.g.*, 12 mm. and not 0·47 inches).

Mr. ALEXANDER RUSSELL stated that Mr. Upson's paper would be extremely useful to all engaged in research in connection with the electric arc. He agreed with the author that coal-gas was very unsuitable for experiments with the arc. He had recently been experimenting with high-voltage alternating arcs in coal-gas, and in most cases the enclosing vessel was soon filled with black cobwebs. When, however, the high-voltage high-frequency arc between iron-iron electrodes was shunted by a Leyden jar in series with a small coil of wire the discharge between the electrodes became simply a torrent of sparks, and no appreciable quantity of soot was formed. The difficulty the author experienced in certain cases in obtaining an arc was due probably to the low voltages used. When high voltages are applied it is easy enough to maintain an arc. More experimental research was wanted on the upper part of the statical characteristic curve of the arc. A good deal of exploration has already been made in this direction in Dr. Simon's Laboratory at Göttingen with the help of a motor generator from which three or four ampères of direct current can be obtained at 5000 volts. The results already obtained were of great importance. The success of the statical characteristic method as an instrument of research was mainly due to the care with which Mrs. Aryton had specified the method of obtaining the curve. He hoped that Mr. Upson would make further researches at high voltages.

Dr. FLEMING congratulated Mr. Upson on his paper, and said that it represented a considerable amount of careful work, and even if all the conclusions to be drawn from it were not yet absolutely clear, it would furnish a statement of facts which would assist in future theorising. He said

that the interesting part to him at the moment was the difference between the form of the volt-ampère characteristics for the carbon-carbon arc in air and the metal-carbon arc in hydrogen, but on that matter he would defer his remarks until he had shown some other experiments.

Mr. Upson, in reply, stated that the primary object of the paper was to compare metal arcs with carbon arcs. He had also performed some experiments with charge of voltage and variations in the length of burning of the arc, and he hoped to carry out a series of experiments using high voltages.

Experiments were then exhibited by Dr. J. A. Fleming, F.R.S., with the Poulsen Arc as a means of obtaining continuous electrical oscillations, repeating some of those shown by him at the Royal Institution on May 24th last.

Dr. Fleming showed and described an apparatus for forming an electric arc in an atmosphere of coal-gas between a carbon rod kept in slow rotation and a cooled copper anode, the arc being formed in a magnetic field of 600 to 1000 C.G.S. units. The arc was supplied with continuous current at a pressure of 400—500 volts. A condenser of 0·003 mfd. capacity in series with an inductance of 200,000 cm. was shunted across the arc, and experiments shown to prove the existence of high frequency oscillations in the condenser circuit. A long resonance helix of insulated wire was then joined to the condenser circuit, and when tuned to it created a powerful high frequency field round it in which vacuum tubes glowed brilliantly. By vibrating or rotating a Neon vacuum-tube of spectrum type near the helix, and showing that the band or disk of light was cut up by dark spaces, Dr. Fleming supported the contention that the oscillations so produced are not absolutely uninterrupted but cut up into groups. Another experiment was shown to confirm this. The oscillations produced by the arc in one circuit were caused to create secondary oscillations in another circuit in which was a condenser shunted by one of Dr. Fleming's oscillation valves and a telephone. The valve rectifies the secondary oscillations, and if they were absolutely continuous the telephone would be traversed by an uninterrupted direct current. But as a fact a discontinuous sound is heard in the telephone which can arise if the primary oscillations come in batches or groups.

Dr. Fleming then gave some figures showing the kind of values obtained for the efficiency of transformation of continuous to oscillatory current by the arc, and compared them with similar measurements for the spark method. He concluded with some discussion of the *modus operandi* of the metal-carbon arc in the production of oscillations in a shunt circuit containing capacity and inductance. In the first case the curve was (as shown from Mr. Upson's diagrams) much steeper than in the second. This implied that the same amount of energy could be conveyed to the oscillatory circuit by means of a condenser of smaller capacity, and therefore give higher frequency. This was confirmed by the fact that the curve for small currents in the case of the carbon arc in air was steeper than for large currents, and it was found that a Duddell carbon arc could give high frequency oscillations when actuated with small currents. He thought that there was still much work to be done before the whole of the phenomena of the oscillatory arc were understood.

Mr. W. Duddell expressed his interest in the experiments, especially those in which it was shown that the oscillations were broken up into groups. He pointed out, however, that it was possible to obtain continuous oscillations with a musical arc using high frequencies. The question as to the measurement of the power put into the Poulsen arc was of great interest, as also was the question as to the amount of power which could be taken from the secondary without stopping the arc. He questioned Dr. Fleming's statement that the power put into the arc was equal to the product "AV," and said that the power should be measured with a wattmeter.

Mr. A. Campbell remarked that Mr. Altberg in Odessa, had lately shown that sparks of high oscillation frequency produce actual air vibrations of the same frequency, and by measuring the wave lengths of these air vibrations by diffraction methods he had been able to determine the high frequency.

Dr. Fleming, in reply, said he was prepared to accept Mr. Duddell's criticism that the power put into the Poulsen arc should be measured with the wattmeter. The really important matter, however, was the reason why the metal-carbon arc in coal-gas could produce oscillations of so much higher frequency than the carbon arc in air. This he thought was intimately connected with the slope of the characteristic curve.

Mr. Rollo Appleyard exhibited a Direct-reading Conductivity Bridge for testing rods of steel or other material, where there is considerable range of conductivity between successive specimens, and where it is necessary to eliminate the resistance of end contacts.

The instrument is provided with two scales and with corresponding sliders. By setting one of the sliders with reference to its scale, compensation is made for any small difference of diameter or of mass between the standard rod and a test rod. The second slider is then adjusted to the position of balance, and the conductivity is read off the second scale as a percentage, according to Matthiessen's standard, or in terms of any desired unit. All arithmetic is avoided, and the results are obtained at the rate of two or three a minute. Mr. Appleyard gave the equations for the calibration of the scales, and showed that the errors involved by the use of the compensation scales were for practical purposes negligible.

Mr. A. Campbell said he had used the author's conductometer and testified to its convenience. He objected, however, to the measurement of conductivity in terms of Matthiessen's standard, and suggested that for work with nickel steels, &c., the bridge should be graduated in resistivities.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 23, June 10, 1907.

Oxidising and Decolorising Properties of Graphite.—Henri Louis Dejust.—To measure the decolorising power of graphite the author shook 1 grm. of it with 42 cc. of a solution of litmus containing 9·8 grms. of extract per litre at 100°. After shaking for thirty seconds it was filtered, and the colours of the filtrates compared with one another. The same graphite after purification (reducing its carbon to 93·1 per cent) produced less decoloration. If the medium in which the operation takes place is acid, neutral, or basic the effect is unaltered. With animal black, however, in a neutral or acid solution the decoloration is total, while in a basic solution it is less than when purified graphite is used. Graphite has an oxidising action like that of animal black. A solution of paraphenylene diamine left in air in contact with graphite in the cold turns brown, and this effect is accelerated by heating. It also decolorises a solution of litmus in absence of air; for example, when a flask of the solution which has been boiled is completely filled.

Nickel Acetate as a New Type of Oxidiser for Hydroquinone.—André Job.—Neutral acetate of cobalt brings about the oxidation of hydroquinone, but its activity soon diminishes and finally disappears. It is, however, easy to prepare an active nickel acetate which readily effects the oxidation of hydroquinone, surpassing even manganese acetate in this respect. It is prepared by

heating chemically pure nickel acetate for some time to 100°, when it loses acetic acid, but remains entirely soluble in water. The activity of both manganese and nickel acetate can be diminished by diminishing the amount present and also by adding acetic acid. With manganese if the activity is reduced by dilution, it is also rendered less lasting, while when acid is added the activity becomes more stable and remains constant from the commencement of the action. With nickel, on the other hand, a rapid diminution of the velocity of the action is caused, whichever way the activity is reduced. This is because heated nickel acetate has already lost acetic acid and owes its activity only to the free hydrate. The neutral manganese acetate is made active by the small amount of hydrate which its hydrolysis furnishes. The feeble acidity of the hydroquinone is sufficient to stop this hydrolysis, and the effect is more appreciable the smaller the amount of manganese present, but if the hydrolysis has already been checked by the addition of free acetic acid the effect of the hydroquinone is negligible. In the case of nickel, the addition of acetic acid only neutralises a little hydrate. Thus, nickel acetate modified by heat constitutes a new type of oxydase for hydroquinone, in which the influence of the metallic hydrate can be isolated and measured, by comparing the activity of the neutral acetate of nickel with that of modified acetate in which the amount of free hydrate is known.

Compounds of Hypovanadic Acid with some Oxygenated Acids.—Gustave Gain.—Hydrated hypovanadic acid, $V_2O_4.2H_2O$, dissolves in a dilute solution of selenic acid, giving a blue crystalline powder, $V_2O_4.3{\cdot}5SeO_3.7H_2O$. When excess of selenic acid is used a selenate is deposited, but with much more difficulty. It has the composition $V_2O_4.5SeO_3.10H_2O$. The corresponding sulphates differ from these only in the number of molecules of water, being $V_2O_4.3{\cdot}5SO_3.10H_2O$ and $V_2O_4.5SO_3.12H_2O$. When phosphoric acid is substituted for selenic acid the compounds formed are $V_2O_4.2P_2O_5.6H_2O$ and $V_2O_4.3P_2O_5.10H_2O$, and with arsenic acid the product is $V_2O_4.3As_2O_5.6H_2O$.

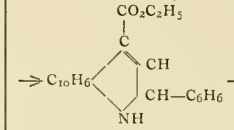
Relations between the Diagram of Binary Alloys and their Malleability.—Léon Guillet.—I. When the metals are deposited in a pure state, if they are both malleable, so are all the alloys; if neither metal is malleable, no malleable alloy can be prepared; and if one metal is malleable and the other is not, the malleability of the alloys depends upon that of the eutectic. II. When the metals are only miscible in the solid state in the neighbourhood of the pure metals, and do not form combinations, if one of the metals is malleable, the solid solution rich in this metal is always malleable. III. When the metals form combinations or solid solutions which solidify at a constant temperature, only those alloys which are at the extremities of the diagram are malleable. IV. When the alloys form solid solutions which decompose before liquefying, an alloy formed of a pure malleable metal, or of a solid solution very rich in this metal and a compound, will possess only feeble malleability. An alloy formed of two solid solutions, one of them rich in malleable metal, is only malleable if the proportions of the second are low. V. When the metals are miscible in all proportions, if one metal is malleable, so are all the alloys; the only exception to this rule is the iron-manganese alloy, but the manganese employed is very impure.

Mechanism of the Synthesis of Quinoline Derivatives.—L. J. Simon and Ch. Mauguin.—When pyruvic acid, CH_3COCO_2H, acts in alcoholic solution on a primary aromatic base in presence of an aldehyde a phenylquinolinic acid is obtained:—

$$C_{10}H_7NH_2 + CH_3COCO_2H + C_6H_5COH = 2H + H_2O + C_{20}H_{10}O_4N$$

(Döbner). The authors have investigated the mechanism of this reaction, using chloroform or benzene as solvent and substituting benzylidene β-naphthylamine for the β-naphthylamine. They have thus obtained the following products:—(1) Methylnaphthoquinoline carboxylic acid; (2) phenylnaphthoquinoline carboxylic acid; (3) tetrahydrophenylnaphthoquinoline carboxylic acid; (4) benzylnaphthylamine. Apparently an intermediate product is formed and the transformations can be represented by the equations:—

$$CH_3{-}CO{-}CO_2C_2H_5 + C_{10}H_7{-}N{=}CH{-}C_6H_5 = CO_2C_2H_5{-}CO{-}CH_2 \rightarrow C_{10}H_7{-}NH{-}CH{-}C_6H_5$$



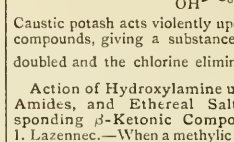
Ether Function of Diphenol.—R. Delange.—The group $-O-\!>\!CCl_2$ is easily transformed into $-O-\!>\!CO$ by the action of cold water. When cold water acts on tetrachloride of piperonal a new compound is obtained which, when boiled with water or dilute acids, undergoes the following reaction:—

$$CO{<}^{O}_{O}{>}C_6H_3{-}CHCl_2 + 2H_2O = {=}{}^{OH}_{OH}{>}C_6H_3{-}CHO + CO_2 + 2HCl.$$

Caustic potash acts violently upon the dichloromethylenic compounds, giving a substance in which the molecule is doubled and the chlorine eliminated, $-O-\!>\!C = C{<}^{O-}_{O-}$.

Action of Hydroxylamine upon Nitriles, Acetylenic Amides, and Ethereal Salts, and on the corresponding β-Ketonic Compounds.—Ch. Moureu and I. Lazennec.—When a methylic solution of hydroxylamine, separated from its chlorhydrate by sodium methylate, acts on phenylpropiolic nitrile a compound, $C_9H_8N_2O$, is formed. When this is boiled with concentrated hydrochloric acid it yields $C_9H_7NO_2$. This appears to be formed as follows:—

$$C_6H_5{-}C{\equiv}C{-}CONH_2 \quad C_6H_5{-}C{=}CH{-}CONH_2$$



The substance $C_9H_8N_2O$ is 3-phenyl-5-iso-azolonimine. Unsubstituted β-ketonic nitriles give the same products of condensation with hydroxylamine, viz., cyclic compounds containing two atoms of nitrogen. Acetylenic amides and ethereal salts give the same compounds as are obtained with the corresponding amides and β-ketonic ethereal salts. These derivatives are isoxazolones.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. G. Jamieson, C.M.G., Dr. S. Shore Nightingale, Mr. W. Stone, Mr. H. S. Stoneham, and Mr. E. Turk were elected Members.

ERRATUM.—Vol. xcv., p. 301, col. 1, line 31 from bottom, *for* "6L8" *read* "bL8."

THE CHEMICAL NEWS.

Vol. XCVI., No. 2485.

RADIO-ACTIVE LEAD AND GRIGNARD'S REACTION.

By K. A. HOFMANN and V. WÖLFL.

Radio-active lead has recently been made the subject of exhaustive physical investigations. In agreement with the qualitative results obtained by Hofmann (*Ann. d. Physik*, 1904, [4], xv., 615), Gonder and Wolff, Stefan Meyer (*Wiener Sitzungsberichte*, July, 1905, cxiv., ii.*a*, and *Jahrb. der Radio aktivität und Electronik*, 1906, iii., 385), and Egon v. Schweidler proved by quantitative measurements that there is present in radio lead a substance which does not emit rays, but suffers a transformation (Period of decay of activity to the half value = about 40 years). This is called RaD from its position in the decay series, and from it is developed directly a β-radiating substance RaE_2, with the half-constant of 4·8 days; this in turn passes into RaF, which emits only α-rays, and has a period of decay to the half value = 137 days.

In this series, RaD no radiation $\rightarrow$ RaE_2 no radiation $\rightarrow$ RaE_2 β-radiation $\rightarrow$ RaF α-radiation, is contained the group of the uranium derivatives belonging to the heavy metals, and it forms the end of the radio-active decay of uranium according to Rutherford's hypothesis (*Phil. Mag.*, 1904, viii., 636; *Nature*, 1905, lxxi., 341).

Rutherford, Soddy, and Boltwood assume that the final stable product is ordinary inactive lead, which Hofmann and Strauss (*Berichte*, 1900, xxxiii., 3126), had already detected in uranium minerals, and the amount of which was proved by Boltwood (*Amer. Journ. Science, Silliman*, [4], xxiii., 77), to be proportional to the amount of uranium present in unchanged primary minerals. But when we reflect that, as the decay of the members of the above series proceeds, they become electrochemically more positive (St. Meyer and E. von Schweidler, *Jahrbuch der Radioaktivität und Electronik*, 1906, iii., 395), we shall also include among the products of final decay tellurium (W. Marckwald, *Berichte*, 1902, xxxv., 4239), which is very closely allied to RaF, and the substance similar to platinum which I discovered in the lead of pitchblende, and the spectrum of which shows at least two unknown lines, $\lambda = 4995$ and $\lambda = 2785$.

The aim of our experiments was now to examine as fully as possible the analytical characteristics of RaD compared with those of RaF, in order thus to isolate the separate members.

RaF, radio-tellurium, is, according to Marckwald (*Berichte*, 1902, xxxv., 1239), separated as an electro positive substance from a hydrochloric acid solution of bismuth polonium by means of copper or bismuth. We were convinced that no other substance with a more lasting activity could be isolated from such solutions, for precipitates with equal decay constants were formed on electrochemically different metals.

According to the formula $I = I_0 e^{-\lambda t}$, λ for lead-foil is 0·00521, for silver-foil 0·00515, for lead-foil 0·00516, for platinum foil 0·00516. Hence the calculated value for the time required for the half decay is 134·4 days. Marckwald (*Jahrbuch der Radioaktivität und Elektronik*, 1905, ii., 136), found for radio-tellurium 139·6 days; according to Stefan Meyer (*Wiener Sitzungsberichte*, 1906, cxv., ii.*a*, 63) and Egon v. Schweidler the time is 136·5 days.

Even in a solution of radio-lead chloride containing RaD with RaF, only RaF can be detected as a more lasting principle giving α-rays.

We found for λ from the decay equation $I = I_0 e^{-\lambda t}$, for lead λ 0·0051, for copper $\lambda = 0·0053$, for silver $\lambda = 0·0051$; thus the mean value was $\lambda = 0·00516$, which is the same as with bismuth-polonium solution.

RaF is chemically different from bismuth, for Marckwald (*Berichte*, 1902, xxxv., 4239), states that it is closely analogous to tellurium. We succeeded in obtaining from the mother-liquors of bismuth-free radio-lead chloride solution by means of an alcoholic mixture of hydrochloric and sulphuric acids, a substance which emitted much α radiation; this substance agreed analytically with lead, even to the solubility of its sulphate; and according to Prof. Exner its spectrum showed only lead lines. The original strength was found by Egon v. Schweidler to be 3000 uranium units when the surface was the same; since 1·5 grms. of uranium corresponded to 0·005 grm. of the substance, the activity of a given weight must be considerably greater. For this preparation, which was undoubtedly free from bismuth, Stefan Meyer and E. v. Schweidler (*Wiener Sitzungsberichte*, 1906, cxv., ii.*a*, 63), found 134·5 days for the period of decay to the half value.

As RaF in bismuth-polonium follows bismuth as oxychloride and oxynitrate as the only α-active constituent, which has recently been proved by Sk. Curie (*Comptes Rendus*, cxlii., 273), it follows that RaF has analytically the mixed characteristics of bismuth, lead, and tellurium, if we do not prefer to assume that RaF is allied to these elements in the same way as a member of the sulphur group. In our opinion this is shown by the fact which we have already reported (*Ann. d. Physik*, 1904, iv., xv., 625), that even noble metals such as palladium, platinum, iridium, and rhodium, take up RaF readily from solutions, which cannot be interpreted to mean that these metals separate RaF electrochemically, for then it would have to be still more electro-positive than these last members of the potential series. Also when radio-lead acetate or nitrate is electrolysed, RaF is separated not only at the calthode (see also St. Meyer and E. v. Schweidler, "Lieben-Festschrift," 404, and Hofmann's earlier statement, *Ann. d. Physik*, 1904, xv., 621), but also at the anode in considerable quantities—in one operation up to as much as 300 uranium units; but this amphoteric behaviour may be caused by the formation of a higher oxide.

In electrolytic, electrochemical, and hydrolytic processes, RaF is followed by the β-radiating (F. Giesel, *Berichte*, 1906, xxxix., 780), but extremely rapidly decaying RaE_2, with the period of decay to the half value of 4·8 days. (H. v. Meyer and E. v. Schweidler, "Lieben-Festschrift," 408).

Our recent experiments were aimed chiefly at isolating RaD, the comparatively long existence of which (period of decay to the half value = 40 years), renders possible a more detailed chemical characterisation. Although the difficulties of separation from inactive lead are extraordinarily great, we discovered several ways of effecting it.

The partial crystallisation (Hofmann, *Ann. d. Phys.*, 1904, xv., 621), of the chloride from water, or better, from strong hydrochloric acid, leads to an accumulation of RaD in the first, difficultly soluble parts, while RaE and RaF pass into the mother-liquors.

The distillation of radio-active lead chloride in presence of some ammonium chloride is much quicker; RaD, as well as RaE and RaF, then volatilises more easily than ordinary lead chloride. If RaE and RaF are removed from the distillate by repeated crystallisation from strong hydrochloric acid, and the first crystals are purified by precipitation from aqueous solution with sulphuretted hydrogen, the sulphide is at first hardly active, but gradually develops α and β activity in a far higher degree than the original material. In the electrolysis of nitrate and acetate solutions the RaD goes to a slight extent to the anode, and is much concentrated at the cathode if this consists of mercury. A preparation as sulphate enclosed in a completely exhausted capillary after a period of several months showed distinctly the helium lines $\lambda = 587·5$, 501·6, 447·1, while with RaE and RaF all our experiments in this direction

have so far given absolutely no result. (See also Grienacher, *Naturwissenschaftl. Rundschau*, 1906, xxi., 671; we shall return to this point elsewhere). No radium emanation could be detected in any preparation.

If zinc is allowed to act for some time on fused radio-lead chloride, RaD, RaE, and RaF accumulate in the metallic regulus (the two latter very strongly), while only RaE and RaF are reduced when it is fused with silver foil.

But all these methods lead ultimately to the formation of preparations in which the ratio of RaD to inactive lead cannot be altered to such an extent that the isolation of RaD seems possible.

Much better results are obtained by a method which we have worked out with G. Ebert, and which is of general chemical interest, namely, the conversion of lead chloride into lead tetraphenyl, using phenyl magnesium bromide.

Magnesium shavings are rendered active not with iodine, as usual, but with a few drops of bromine; then bromo-benzene in absolute ether is added, and after the phenyl magnesium bromide is formed it is mixed with lead chloride, powdered as finely as possible, made to a paste with benzene, and thoroughly dried. The mass soon becomes black, owing to the separation of metal, and after shaking for several hours the magnesium compound can no longer be used to form lead phenyl. The tetra- and not the di-phenyl compound is thus prepared, half of the lead separating as metal. After filtering the residue is washed with benzene, and all the filtrate evaporated to one-third, shaken up with water, and then again dried and filtered; the benzene solution is then evaporated to crystallisation. The di-phenyl must be removed from the mixture of crystals by ligroin or gasoline, and the residue of lead phenyl again re-crystallised from a little benzene. The crystals melt at 229° and consist of colourless, double refracting prisms, glittering like silk or diamonds. The end surfaces are inclined at about 120° to the prism edges.

0·2417 grm. of substance after repeated evaporation with sulphuric acid: 0·1394 grm. $PbSO_4$. 0·1716 grm. substance: 0·3550 grm. CO_2; 0·0648 grm. H_2O.

$PbC_{24}H_{20}$: Calculated—Pb, 40·03; C, 56·14; H, 3·90.
Found—Pb, 39·40; C, 56·35; H, 4·19.

Clearly this lead tetraphenyl is identical with the substance obtained by Polis (*Berichte*, 1887, xx., 717, 3331), by boiling lead sodium with bromobenzene and acetic ether for 3 days.

The use of phenyl magnesium bromide in our method, apart from the very simple process and the good yield (if the reagents are quite dry), has the great advantage that the lead chloride is used directly and is not exposed to the risk of loss on converting it into the metal, which is a very important point when the cost of concentrated radio-lead chloride is taken into account. Also this application of Grignard's reaction, as our preliminary experiments showed, can be used very generally in order to obtain phenyl compounds or their ethereal solutions in the cases when the metals yield no such compounds ($BiCl_3$, $SnCl_4$, and $SiCl_4$ readily form phenyl compounds). In particular, the noble metals, gold, silver, and platinum, can be converted into beautiful coloured ethersols, upon which a full report will shortly be made.

Lead tetraphenyl itself calls for closer investigation from many points of view. Thus when the crystals are dissolved in a mixture of 3 volumes of concentrated sulphuric acid to 1 volume of fuming nitric acid, an intense brownish-red colouration appears, afterwards changing to cherry-red. If after longer action this is precipitated with much water at the ordinary temperature, fine white pointed prisms united in branching feathery formations crystallise; these swell up on heating, giving a strong smell like nitro-benzene.

The method of phenylation is too dear for working up lead chloride which has not been concentrated, but it presents very considerable advantages in removing the ordinary inactive lead from RaD preparations, enriched by distillation with ammonium chloride, electrolysis, or by crystallisation.

RaF, in consequence of a secondary reduction, goes into the residue, RaD also for the most part remains behind, RaE is found in the deposit of magnesia separating on shaking up the benzene solution with water, and very feebly active lead goes over into the phenyl compound. The following table shows the result of the concentration of RaD.

Uranium units.

I.

Sulphate from the residue (after removing RaF as completely as possible), three weeks after separation	15
Sulphate from the residue six weeks after separation	36
Sulphate from the phenyl compound three weeks after separation	2
Sulphate from the phenyl compound six weeks after separation	0·8

II.

Sulphate from the residue (after removing RaF as completely as possible), three weeks after separation	23
Sulphate from the residue six weeks after separation	42
Sulphate from the phenyl compound three weeks after separation	7
Sulphate from the phenyl compound six weeks after separation	0·5

Even if these numbers are not absolutely valid owing to the amounts of RaE_1 and RaE_2 which are not taken into account, they show that in the part not converted into the phenyl compound (the residue), the principle producing activity (which must be the RaD) appears very decidedly concentrated. If the residue is again treated as chloride with phenyl magnesium bromide in ether and benzene, the oxygen of the air takes part in the reaction and an intense fuchsine-red colouration is produced, which is destroyed by moisture.

The aim of our next experiments will be to investigate the subject more fully in the directions we have indicated in this paper.—*Berichte*, 1907, xl., 2425.

Chemistry of Silicon.—A. Ladenburg.—If silicon tetraphenyl is warmed on a water-bath with bromine and then heated in a tube for eight to ten hours with 10 per cent bromine to 150°, the following reaction occurs:—$Si(C_6H_5)_4 + Br_2 = C_6H_5Br + Si(C_6H_5)_3Br$. The contents of the tube are washed out with ligroin, which is evaporated off on the water-bath, and the bromo-benzene is driven off *in vacuo*. The impure bromide crystallises out on cooling, and may be purified by dissolving in ether. Tri-phenyl silicon bromide is a colourless crystalline substance fuming in air and melting at 118—120°. When it is heated with potash solution to 120° it yields the triphenyl silicol, $Si(C_6H_5)_3OH$. When this silicol is dissolved in fuming sulphuric acid, the liquid is poured into cold water and neutralised with barium carbonate, after warming for some time crystals of the barium salt of the trisulpho acid of tri-phenyl silicol separate: $Si(C_6H_4SO_3Ba)_3OH$. Diphenyl silicon dibromide, $Si(C_6H_5)_2Br_2$, cannot be prepared directly from silicon tetraphenyl, but the monobromide when heated with bromine yields an oil from which it may be separated. Zinc ethyl acts upon the dibromide giving silicon diphenyl diethyl, and with water the dibromide gives an oil which has approximately the composition represented by the formula $Si(C_6H_5)_2O$. Zinc ethyl with triphenyl silicon bromide gives two compounds, triphenyl silicon hydride, $Si(C_6H_5)_3H$, and ethyl triphenyl silicon.—*Berichte*, xl., No. 9.

CONTRIBUTIONS TO THE CHEMISTRY OF GOLD.*

By F. H. CAMPBELL, M.Sc. (Melbourne).

That revision of and additions to our knowledge of the chemistry of gold is necessary is obvious to any one who refers to the literature of the subject. In many cases different investigators have obtained contradictory results, and other observations have been recorded which have not been contradicted solely because the work has never been repeated.

In any case, investigations in which the methods of physical chemistry are applied are entirely wanting. It was a consideration of these facts which led to the following research. The main part of the work deals with the halogen compounds, but in addition the normal potential of $Au^{\cdot}$ ions was determined.

The Properties of AuI.

This substance has long been known, having been prepared indirectly by Fordos and others (*Journ. Pharm.*, xxvii., 653; *Comptes Rendus*, cxxxix., p. 733). It was first synthesised from its elements by Meyer and obtained in a crystalline form. The method used which gave the largest yield of crystals was to shake precipitated gold with a solution of iodine in KI; after shaking had been continued for from sixteen to twenty-four hours, crystals were observed to have formed. These were lemon-yellow in colour. The temperature of the thermostat was 25° C.

The dissociation pressure of AuI must be smaller than the normal pressure of iodine at the same temperature, since had it been greater the substances would not have united. It remained to determine with what pressure of iodine this substance and gold are in equilibrium.

This equilibrium pressure can be approached from both sides; if metallic gold is brought into contact with iodine, the pressure of which is greater than that of AuI, the substances will unite until the pressure reaches the equilibrium value; on the other hand, AuI, when brought into a space in which the pressure is less than this pressure, will dissociate until equilibrium is established as before.

Since, as will be shown, this pressure at 25° is but little below that of pure iodine, the fact that the aurous iodide decomposes rapidly into its elements when exposed to the air is explained.

As in the case of the dissociation of $CaCO_3$, so in the action $2AuI \rightleftarrows 2Au + I_2$ we have to do with a univariant system consisting of the two solid phases, AuI and Au, and the gaseous I_2. There is only one variable, namely, the pressure of iodine, which is dependent on the temperature.

The method of experiment was similar to that used by Stromholm, Hamburger and Abegg, and Maitland and Abegg for the formation of various polyiodides (*Journ. Prakt. Chem.*, lxvi., 67; *Zeit. Anorg. Chem.*, 1906, xlix., p. 341). The iodine was dissolved in CCl_4, in which AuI, as well as Au, are insoluble, and in which iodine is in the same state of molecular aggregation as it is in the gas form; hence according to Henry's law the gaseous pressure of iodine above the solution is directly proportional to the concentration of the dissolved iodine.

Solutions of iodine of varying concentrations were placed in bottles having well-fitting glass stoppers together with finely divided gold. After having covered the stoppers with rubber caps, the bottles were shaken for seven days in a thermostat at 25° C. Those solutions the original concentration of which did not reach 0·1088 mol. of I_2 per litre, had exactly the same titre afterwards as before, while those with a higher original concentration than this became diluted to 0·1088 mols. per litre. The iodine estimations were performed in the usual way with 0·1*n* $Na_2S_2O_3$, starch being used as an indicator. 1 cc. of the CCl_4 solution was placed in a stoppered bottle so that the two solutions could be shaken together. By this means a sharp end-point could be obtained.

In other cases AuI was prepared by precipitation from $AuCl_3$ solution by means of KI, $AuCl_3$ being always in excess. The mixture of AuI and I_2 thus obtained was washed with cold water and dried with filter-paper before being shaken with a dilute iodine solution. Again the solutions obtained from the first series of experiments were diluted with pure CCl_4. It was found that under the conditions of experiment the action $2Au + I_2 \rightleftarrows 2AuI$ goes at a much greater rate from left to right than the reverse action. For example,—

Table I.—*Action of Iodine in* CCl_4 *on* Au *metal.*

$Na_2S_2O_3$ required by 1 cc. solution.	Duration of experiment.
Cc.	Days.
2·24	0
2·24	3
2·25	10
2·26	16
2·24	30
2·26	60

After each titration 2 cc. of iodine solution, the titre of which was 2·40, was added. This table not only serves to show the great constancy obtained, but also that the action goes comparatively quickly. On the other hand, Table II. shows that when AuI is placed in contact with a dilute iodine solution the action is exceedingly slow.

Table II.—*Action of Solvent* CCl_4 *on* AuI.

$Na_2S_2O_3$ required by 1 cc. solution.	Duration of experiment.
Cc.	Days.
2·03	0
2·08	8
2·10	42
2.11	64

Since in this particular case the amount of AuI originally present was small, the constancy of the last results may be attributed to the total decomposition of this substance.

In another case about 1 grm. of AuI was prepared by precipitation as above. In order to hasten the action various methods were tried; the most effective was found to be to treat the solution for some hours to 55° and then to shake for some days at 25°. From an experiment conducted in this way, the results given in Table III. were obtained.

Table III.

$Na_2S_2O_3$ required by 1 cc. solution	Duration of experiment.
Cc.	Days.
2·08	0
2·14	9
2·21	21

Taking the mean of the values obtained by both methods we find that 1 cc. of the solution requires 2·23 cc. 0·1*n* $Na_2S_2O_3$, so that a solution of iodine in CCl_4 containing 0·1088 mol. I_2 per litre is in equilibrium with gold and AuI at 25°. Under these conditions a saturated solution contains 0·1156 mol. iodine, hence the pressure of gaseous iodine which is in equilibrium with AuI and gold is $\frac{0\cdot1088}{0\cdot1156} = 0\cdot943$ of that of pure iodine.

Therefore any solution of iodine is or is not able to act on gold according to whether it is or is not 0·943 saturated.

* A Paper read before the Faraday Society, May 28, 1907.

The Determination of the Formula of the Double Iodide of Potassium and Gold.

When excess of gold is treated with iodine dissolved in aqueous solutions of KI, part is converted into AuI, which is insoluble, part remains unattacked, while the rest is dissolved.

The action may also be looked at from the point of view of the iodine. Of this, part combines with I′ ions to form I_3' ions, part goes to form AuI, part is used to form a complex gold-containing anion, while the rest, relatively to the other parts very small, remains as free molecular iodine, I_2.

Of the AuI formed part remains insoluble, while the rest combines either with only Iodine ions, I′, to form a complex anion, probably AuI_2', or else with iodine ions, I′, and free iodine, I_2, to form a complex ion, probably AuI_4'; in other words, the complex compound may contain either mono- or tri-valent gold. In order to solve the problem the following experiments were made.

Meyer has shown that AuI is formed under the conditions of experiment, but it was considered advisable to analyse the crystalline substance obtained, since this decomposes rapidly on washing. Exact analysis was not possible. The results obtained, however, left no doubt that the substance obtained is AuI.

It was found that when a glass rod, previously roughened by treatment with HF, and of such a length that it could not move, was placed in the bottle, good crystals were formed upon it. When required for analysis, the crystals were removed, washed with cold water, dried with filter-paper, and transferred to a tared glass tube, the neck of which was then sealed off, the tube and contents were weighed; the neck was next broken and the tube gently heated till iodine vapour ceased to be evolved. After cooling in a desiccator the tube was again weighed.

In one case the following results were obtained:—

Weight of substances before heating ..	0·0012
Weight of substances after heating ..	0·0007
Iodine volatilised	0·0005
Percentage of iodine (found)	41·7
Percentage of iodine (calculated)	39·5

In this case the crystals had evidently not been thoroughly dry, but in any case, owing to the unfortunate necessity of using exceedingly small quantities, a higher degree of accuracy is not to be expected.

It having thus been proved that the solid phases present are Au and AuI we are in a position to say what we have in the two systems present in solution. We have I_2, I′, I_3', Au·, Au··· and the complex ions either AuI_2' or AuI_4'. Of these I_2, Au·, Au··· are present in very small quantity, so that the dissolved gold may be considered as being present completely in the form of complex anion, and we make the assumption that the complexes have only one formula, either $Au^{I}I_2'$ or $Au^{III}I_4'$.

According to the law of mass action,—

$$\frac{(I_2)\cdot(I')}{(I_3')} = Kj;$$

and since—

$$AuI + I' = AuI_2' \quad \text{or} \quad AuI + I' + I_2 = AuI_4',$$

then—

$$\frac{(AuI_2')}{(AuI)(I')} = K_1 \quad \text{or} \quad \frac{(AuI_4')}{(AuI)(I_3')} = \frac{(AuI_4')\cdot Kj}{(AuI)(I_2)(I')} = K_2.$$

(Formulæ in brackets mean their mol. concentrations).

The value of Kj is known from the work of Jakowkin (*Zeit. Phys., Chem.*, xx., 19); it is sufficient to determine its value in the solutions under consideration to ascertain whether ther value K_1 or K_2 is the equilibrium constant among the other constituent of the solution, since Kj and K_1 or K_2 are mutally interdependent. Since this has been proved to be so in another case by Maitland and Abegg, the direct determination of the complex constant K_1 or K_2 was considered to be unnecessary.

The method of procedure was as follows:—Equal quantities of CCl_4 and aqueous KI solutions almost saturated with iodine were placed in bottles in contact with excess of pure precipitated gold. The mixture was then shaken in a thermostat at 25° until equilibrium was reached, which happened in seven or eight days. The course of the reaction was followed by pipetting out quantities of 1 cc. of the CCl_4 solution and titrating with 0·1*n* $Na_2S_2O_3$. When the duration of the experiment had been determined, only one preliminary estimation—on the sixth day—was performed.

Equilibrium having been reached, 5 cc. of the CCl_4 solution was pipetted out and titrated as before; the value obtained was divided by the distribution coefficient of iodine between CCl_4 and water at 25°, namely 85; this gave the quantity of I_2 present in the aqueous solution.

5 cc. of the aqueous solution were evaporated to dryness in a porcelain dish over a water-bath, the brown residue was further heated over a small flame until the evolution of iodine ceased, the residue was then treated with water and the gold was finally washed on a small ashless filter. When pure the paper was dried and burnt and the residual gold weighed. From its quantity the quantity of iodine combined with gold was calculated.

A further portion of 5 cc. of the aqueous solution was taken for the determination of the total titratable iodine, that is I_2 (giving 2I), I_3' (giving 2I), AuI_2' (giving 1I besides gold), and AuI_4' (giving 3I besides gold). It was found that direct titration of the solution gave unsatisfactory results, owing to a reaction between gold and $Na_2S_2O_3$. The difficulty was overcome by distilling the iodine into a known volume of 0·1*n* $Na_2S_2O_3$ and titrating back with 0·1*n* iodine solution.

In order to determine Kj we use the value for the concentration of I_2 found as described above; the concentration of I_3' is obtained by subtracting from the total titratable iodine in aqueous solution the amount of free I_2 and the amount of iodine combined with gold, while the concentration of I′ is obtained by subtracting I_3' from the concentration of I′ which was originally in solution.

Jakowkin obtained for Kj values varying between $0{\cdot}77\times10^{-3}$ and $1{\cdot}4\times10^{-3}$. It will be seen from Table IV. that the values obtained for Kj, though a little too high, agree fairly well with those of Jakowkin when the gold is assumed to enter the complex in the monovalent condition, while when the presence of trivalent gold is assumed the constant is not at all concordant with that of Jakowkin. The values vary in the same direction as those of Jakowkin, the value of Kj is lower in the more concentrated solutions than in the dilute ones. The variation of the free iodine as shown in column V. was only slight in our experiments. As the comparison between the above formulæ for K_1 and K_2 shows, a greater variation of the free iodine would give another good way to show that our conclusion is right.

The Properties of Aurous Chloride.

The literature of AuCl is scanty and contains many contradictory statements, so the substance was prepared and examined.

The method of preparation was the usual one. Pure, dry $AuCl_3$ was prepared by passing over pure dry gold chlorine purified by passing through $CuSO_4$ solution, and dried by passing through two wash-bottles containing concentrated sulphuric acid, and a tower containing pumice soaked in sulphuric acid. The temperature was kept between 200° and 220°.

The course of the action was followed by weighing the tube containing the gold or the chlorine as the case might be. It was found that though the absorption of chlorine was at first rapid, it afterwards became exceedingly slow, and in no case was pure $AuCl_3$ obtained. Since the presence of AuCl or Au, the only possible impurities, could not have any disturbing effects at a later stage, special measures to drive the chlorination to completion were not taken.

TABLE IV.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
							For AuI_3:			For AuI_3:	
No.	Mol. KI per litre water.	Atoms iodine per litre water, "titratable iodine."	Mol. gold per litre water.	Mol. iodine per litre water, "free iodine." VI. $\times \frac{1}{85}$.	Mol. iodine per litre CCl_4. (*a*)	III.$-\frac{1}{2}$IV. Mol. I_2+I_3' per litre.	VII.$-$V. Mol. I_3 per litre.	(II.$-$VIII.)$\times$V. VIII. $=$ Kj.	III.$-\frac{1}{2}$IV. Mol. I_2+I_3' per litre.	X.$-$V. Mol. I_3' per litre.	(II.$-$XI.)$-$V. XI. $=$ Kj.
1.	0·1009	0·0842	0·0089	$1·09 \times 10^{-3}$	0·0932	0·0376	0·0365	$1·92 \times 10^{-3}$	0·0288	0·0277	$2·89 \times 10^{-3}$
2.	0·1009	0·0964	0·0106	1·13 ,,	0·0962	0·0429	0·0418	1·59 ,,	0·0323	0·0312	2·52 ,,
3.	0·1009	0·0910	0·0091	1·07 ,,	0·0912	0·0409	0·0399	1·63 ,,	0·0318	0·0308	2·43 ,,
4.	0·1009	0·0970	0·0099	1·07 ,,	0·0907	0·0435	0·0425	1·47 ,,	0·0336	0·0326	2·24 ,,
5.	0·2508	0·2616	0·0290	1·16 ,,	0·0985	0·1163	0·1152	1·36 ,,	0·0873	0·0862	2·21 ,,
6.	0·2508	0·2556	0·0297	1·06 ,,	0·0902	0·1129	0·1119	1·31 ,,	0·0832	0·0822	2·17 ,,
7.	0·4038	0·3839	0·0505	1·03 ,,	0·0882	0·1637	0·1627	1·52 ,,	0·1072	0·1062	2·88 ,,
8.	0·4038	0·4009	0·0489	1·10 ,,	0·0942	0·1760	0·1749	1·44 ,,	0·1271	0·1260	2·42 ,,
9.	0·4038	0·3959	0·0522	1·12 ,,	0·0952	0·1718	0·1707	1·53 ,,	0·1196	0·1185	2·69 ,,
10.	1·0096	0·9482	0·1199	0·96 ,,	0·0817	0·4142	0·4132	1·39 ,,	0·2943	0·2933	2·34 ,,
11.	1·0096	1·1111	0·1142	1·07 ,,	0·0912	0·4984	0·4974	1·10 ,,	0·3842	0·3832	1·75 ,,

(*a*) Since 0·1088 is the lowest possible concentration for the stability of AuI, as shown above, it was here in an unstable condition, which could be realised because of the great slowness of the AuI decomposition.

The substance obtained in this way was a dark red crystalline mass, and needle-like crystals of the same colour always formed in the cooler parts of the tube.

The temperature was allowed to fall to between 170° and 180°, and was kept between these limits during the subsequent dechlorination. The tube used in these operations was of such a kind that during heating it could be almost evacuated by means of a suction pump. The removal of the evolved chlorine was facilitated by the passing of a very slow stream of dry air. By this means 4 to 5 grms. of $AuCl_3$ could be converted into AuCl in seven or eight hours. The dechlorination was checked by weighing, and the action was stopped when the weight was approximately that theoretically required for AuCl. The temperatures given by different authors as the most suitable for the formation of AuCl vary between 120° and 200°. With respect to the lower temperatures it may be stated that the crystals which, as was mentioned, formed in the upper part of the tube, did not change colour nor lose their crystalline form as did those in the more strongly heated part of the tube. This would seem to show that at temperatures below 140° to 150° the rate of reaction is exceedingly slow.

The substance so obtained was washed with ether until the last washings showed no trace of colour, the solution of $AuCl_3$ in ether being of a strong yellow colour. It was found that unless the ether had been distilled over sodium a short time before use, it was impossible to wash the AuCl out, thus showing the extreme ease with which water reacts with AuCl.

It was found that when a portion of the substance had been washed pure with ether and was allowed to stand in a stoppered bottle for a day, it again showed evidence of the presence of $AuCl_3$ on being treated with ether. Since the reaction might have been due to the presence of traces of water, fresh experiments were made. The substance was washed as before, and when clean placed in a desiccator containing phosphorus pentoxide. After two days the presence of $AuCl_3$ was obvious when ether was placed in the tube. It was thus shown that the action $3AuCl = AuCl_3 + 2Au$ takes place at ordinary temperatures and in absence of water.

As is to be expected this action goes on rapidly at higher temperatures. The substance when placed in a tube, sealed up and heated, always gave a red sublimate of $AuCl_3$, though proved to be free of this substance by the ether test immediately before experiment.

Dry chlorine and AuCl combine readily at ordinary temperatures to form $AuCl_3$:—$AuCl + Cl_2 = AuCl_3$.

AuCl was placed in a small bulb to which was attached a capillary tube containing a thread of concentrated H_2SO_4, the whole apparatus was filled with pure dry chlorine, and allowed to stand. A steady decrease in volume took place, shown by the movement of the manometer thread; that $AuCl_3$ was formed was shown by heating the substance, when the quantity of $AuCl_3$ which sublimed was much larger than could be accounted for by the decomposition of the AuCl.

The Properties of Aurous Bromide.

AuBr is readily prepared by gently heating $AuBr_3$. Obtained in this way it is a brown powder. It may also be prepared by simply allowing $AuBr_3$ to stand in the air.

Like the corresponding chloride, AuBr decomposes thus—

$$3AuBr = AuBr_3 + 2Au$$

in a dry atmosphere at ordinary temperature, but to a less extent, while on heating the action is rapid.

That $AuBr_3$ does decompose into AuBr at ordinary temperatures was shown by the fact that the substance took the distinctive colour of AuBr. In other words, the decomposition of $AuBr_3$ to form AuBr takes place more rapidly under the conditions of experiment than does that of AuBr to form $AuBr_3$.

(To be continued).

PREPARATION OF THE ANILINE DERIVATIVES OF SUCCINIC ACID AND OF PHTHALIC ACID.

By J. BISHOP TINGLE and MARSHALL P. CRAM.

In the course of some work on the nitration of certain aniline derivatives, which is being carried out by one of us in conjunction with Mr. F. C. Blanck in the laboratory of the Johns Hopkins University (*Am. Chem. Journ.*, 1906, xxxvi., 605), it was necessary to prepare fairly large quantities of the aniline compounds of succinic and phthalic acids. Some of the methods which we have employed for this purpose differ in certain respects from those described in the literature; in two cases they are entirely new; moreover, they have all proved to be thoroughy satisfactory and adequate for our purpose; consequently it appears to be desirable to place them on record.

Succinanil, $\begin{matrix} CH_2.CO \\ | \\ CH_2.CO \end{matrix}\!\!>\!NC_6H_5$, was prepared essentially according to the method of Menschutkin (*Liebig's Ann. Chem.*, 1872, clxii., 166), but the mixture of acid, 45 grms., and aniline 40 grms., was placed in a small retort and heated for three to four hours, at 140—150°, in a paraffin-bath. By this means the water was steadily eliminated, and there was absolutely none of the "bumping" which was a source of trouble to Menschutkin. As soon as the action is completed, the retort is removed from the bath and quickly heated by a direct flame. A little aniline and water pass over, and then the anil. If the distillation is conducted as rapidly as possible there is no danger of the retort's neck becoming closed. The yield is practically quantitative; from 270 grms. of the acid we obtained 330 grms. of anil, once re-crystallised from alcohol.

The conversion of succinanil into *succinanilic acid*, $C_6H_5NHCOCH_2CH_2COOH$, was carried out according to the directions of Menschutkin (*Liebig's Ann. Chem.*, 1872, clxii., 178), by heating the anil with milk of lime, in slight excess. Vigorous boiling for ten or fifteen minutes is necessary to bring the calcium salt into solution. The crystals which form on cooling are separated, treated with hydrochloric acid, and the precipitated anilic acid is re-crystallised once from water. The yield is 129 grms. of purified material from 200 grms. of anil.

Laurent and Gerhardt discovered *succinanilide*, $C_6H_5NHCOCH_2CH_2CONHC_6H_5$, as a by-product in the preparation of succinanil (*Ann. Chim. Phys.*, 1848, [3], xxiv., 179; *Liebig's Ann. Chem.*, 1848, lxviii., 29). Menschutkin (*Liebig's Ann. Chem.*, 1872, clxii., 187), who repeated their work, found that, contrary to the statement of Laurent and Gerhardt, one re-crystallisation from alcohol was quite inadequate for the purification of the substance. He accomplished this by the use of alcoholic potassium hydroxide, which readily acts on the anil, but leaves the anilide unchanged. The yield is very poor. Laurent and Gerhardt only isolated a "small quantity," and Menschutkin obtained 22 grms. of crude material from 40 grms. of acid and 70 grms. of aniline. We find that the anilide can be easily prepared by heating succinanilic acid, 50 grms., with aniline 40 grms., in a reflux apparatus at 180°, during five working days. The product was treated twice with excess of cold dilute hydrochloric acid to remove the unchanged aniline, and, after being washed with water, was boiled for about five minutes with a clear filtered potassium hydroxide solution, consisting of 12 grms. of stick potash in 250 cc. of 95 per cent alcohol, to dissolve any succinanil and succinanilic acid which might be present. Finally, it was re-crystallised from alcohol. The yield was 17·1 grms. of purified material, *i.e.*, 24·8 per cent of the theoretical quantity. We think that the yield might have been improved by heating the mixture of succinanilic acid and aniline under pressure, but a steel bomb was not available, and the use of sealed tubes would have involved a good deal of extra trouble. Some little time after the completion of this part of our work, Arnold Reissert and Arnold More (*Ber.*, 1906, xxxix., 3300) described a method of preparing malonanilide by boiling ethyl malonate with aniline for a short time, and then distilling off the alcohol as it is produced. They do not appear to have tested the behaviour of ethyl succinate under these conditions. We are indebted to Mr. H. N. Morse for carrying out an experiment with ethyl succinate and aniline, according to the method of Reissert and More. After boiling these substances for about thirty minutes with a reflux condenser, the condenser was reversed and the material slowly distilled. The heat was applied by means of a bath containing sulphuric acid. The distillate consisted chiefly of aniline, in quantity almost equal to that originally used. The residue contained a relatively large amount of ethyl succinate, together with a small quantity of solid. The results of this experiment indicate, therefore, that the procedure of Reissert and More is not applicable to ethyl succinate, and that our method for preparing succinanilide is superior to any which has hitherto been described.

Preparation of the Aniline Derivatives of Phthalic Acid.

Of the various methods which have been suggested for the preparation of *phthalanil*, that of Zincke and Cooksey appeared to us to be the most convenient (*Liebig's Ann. Chem.*, 1889, cclv., 375). It consists in adding the necessary quantity of aniline to a glacial acetic acid solution of phthalic acid, and allowing the mixture to remain for some hours at the ordinary temperature. When we attempted to carry out this experiment we found that the solubility of phthalic acid in glacial acetic acid is so very small, being only about 1·7 grms. in 100 grms. at the ordinary temperature, that the preparation of the quantity of material which we needed would have involved a relatively very large expenditure of time and acetic acid. Our experiments were therefore conducted as follows:—Phthalic acid, 200 grms. = 1 mol. and glacial acetic acid, 500 grms., were mixed, and aniline, 112 grms. = 1 mol., was added. After heating this material on a water-bath during two working days, water was added, and the product filtered. The residue consisted of a mixture which could not be separated by repeated extraction with alcohol. In these circumstances, the portion which had not dissolved in alcohol and the part which deposited on cooling the alcoholic solution were mixed, and boiled for ten minutes with a solution of 20 grms. of dry sodium carbonate in 500 cc. of water. A portion dissolved; the remainder, after being washed and dried, weighed 100 grms. and melted at 203—206°; it was therefore practically pure phthalanil, for which Zincke and Cooksey (*loc. cit.*) gave the melting-point 203° and Döbner 205° (*Liebig's Ann. Chem.*, 1881, ccx., 267). The former chemists omit all reference to the yield which they obtained, whereas the latter reports a "theoretical yield" by the distillation of phthalic anhydride and aniline. The yield by our method, as already noted, is 50 per cent of the phthalic acid employed, and if we were repeating our preparation we should omit the treatment with alcohol and boil the precipitate from the diluted acetic acid directly with sodium carbonate. Even with this simplification our method does not appear to be as good as Döbner's, though it is decidedly superior to that of Zincke and Cooksey. There is no indication in the paper of their reason for ignoring Döbner's method, but they state distinctly that "heating should be avoided." Having obtained all the material which we needed we did not consider it necessary to repeat Döbner's work. If there is ground for distrusting it, then our method appears to be the best and most convenient hitherto suggested for the preparation of phthalanil.

At a later stage of our investigation we found that phthalanilic acid could be easily prepared from its constituents without the use of a solvent. Phthalic acid, 10 grms., and aniline 14·6 grms. = about 2·25 mols., were mixed, and allowed to remain at the ordinary temperature for twenty-two minutes. The flask was found to have become hot, and steam had condensed in its upper portion;

moreover, the mixture had become very stiff. More aniline, 6·7 grms., was now added, and the substance heated on a boiling water-bath. After seven minutes a portion was removed, washed with cold alcohol, and re-crystallised from more alcohol. At first the solution was pink, but it became yellow as the heating continued. The product melted at about 160°, re-solidified, and melted again at 190—195°; it contained a considerable proportion of nitrogen, as shown by the sodium test. A portion which had been washed, but not re-crystallised, behaved in a similar manner. The heating was continued for four hours on the water-bath, and another portion withdrawn; after purification in the manner described it gave the same results. A further five hours' heating, nine hours altogether, gave a product which was chiefly phthalanilic acid, but the alcoholic washings, containing, of course, the excess of aniline, after standing for a time at the ordinary temperature, deposited phthalanil. This is certainly the easiest method known to us for making phthalanilic acid, and the yield appeared to be very good. We did not investigate the matter further because we had already obtained as much of the acid as we required. We refer later to the readiness with which phthalanil is formed from phthalanilic acid in the presence of an excess of aniline.

Phthalanilic acid was obtained without difficulty from phthalanil by the method of Zincke and Cooksey (*Liebig's Ann. Chem.*, 1889, cclv., 375), which consists in treating the phthalanil with alcoholic potassium hydroxide and acidifying the resulting potassium salt. Our product melted at 164°, re-solidified, and melted again at 204°, showing that at its melting-point this acid is changed into phthalanil. The yield was 25·5 grms. of acid from 73 grms. of phthalanil.

We carried out a considerable number of experiments with aniline and phthalic and phthalanilic acids respectively, with the object of preparing *phthalanilide*, either in the manner employed for obtaining succinanilide (see above), or directly from the constituents. It was quickly evident that the anilide is relatively highly unstable, and like the anilic acid, is very readily transformed into the anil. We tried careful regulation of the temperature, with and without the use of aniline in excess. We obtained the phthalanilide in several experiments, but on repeating them it became manifest that this result was dependent on conditions beyond ordinary control, and, consequently, we cannot regard the problem as being solved at all to our satisfaction. We give below a brief description of our experiments. In the preparation of phthalanil by the method of Zincke and Cooksey (*loc. cit.*), we separated the products of the reaction by means of sodium carbonate. On acidification a white precipitate was formed consisting, presumably, of phthalic and phthalanilic acids (see above). This mixture was added to enough aniline to form a stiff paste, and heated on a water-bath for about two weeks. A portion of the product, washed twice with cold dilute hydrochloric acid, and then re-crystallised from alcohol, melted at 230°, which is 1° below the melting-point of phthalanilide. The remainder of the aniline mixture was now heated at 140° for three or four days, and was then found to consist of phthalanil.

In another experiment, phthalic acid, 9 grms., and aniline 22 grms., were heated on the water-bath for two days. The product was purified by means of hydrochloric acid and alcohol, as described above, and melted at 215—220°. The melting-points of phthalanil and of phthalic acid are 203° and 213°, respectively. Boiling for six hours with alcohol, or prolonged heating on the water-bath with an additional quantity of aniline, caused no change in the melting-point of the product. A further 5 grms. of aniline were now added and the mixture heated at 120—130°, for 1·5 days. The product melted at 201—205°, showing it to be, essentially, phthalanil.

Phthalanilic acid, 5 grms., and aniline 12·5 grms., were heated at 120—310° for 1·5 days; the product melted at about 201° and further heating of the mixture at 140—190° produced no decided change in this respect. Additional experiments were made with similar mixtures of phthalanilic acid and aniline, at temperatures ranging from that of the room up to the one given by a boiling water-bath. In some cases the product was re-crystallised from alcohol, in others washed with cold alcohol or with cold hydrochloric acid. The substances obtained consisted either wholly of phthalanil or of mixtures of this with phthalanilic acid; moreover, we found that boiling the alcoholic washings, containing aniline and phthalanilic acid, always resulted in the formation of phthalanil.

A similar series of experiments was carried out with phthalic acid and aniline, but we failed to obtain any of the anilide. We found, however, that phthalanilic acid, as already stated, is easily prepared by simply mixing phthalic acid (1 mol.) with aniline (2·5 mols.) at the ordinary temperature.

We think our results indicate that, although the formation of succinanilic acid and of phthalanilic acid take place in a similar manner, yet in the presence of aniline the further reaction of these substances is quite different, the former yielding succinanilide and the latter phthalanil; moreover, this difference is not by any means simply a question of relative stability at a given temperature, because, as our experiments show, phthalanilic acid is more unstable at the temperature of a boiling water-bath, in the presence of a large excess of aniline, than in its absence. One experiment in support of this has already been given and two others may be cited. Phthalic acid, 10 grms., was mixed with aniline 14·6 grms. = about 2·25 mols., and as it became thick more aniline, 6·7 grms., was added and the mixture heated in an open flask, on the water-bath, for ten hours. After being washed with cold alcohol the solid residue was found to consist of phthalanilic acid. The alcoholic washings containing the aniline, without any further heating, soon deposited phthalanil. During a further five hours' heating the contents of the flask were accidentally allowed to become dry, as the excess of aniline is readily volatile in the steam formed during the reaction. The product was still phthalanilic acid. It was now moistened with aniline, allowed to remain at the ordinary temperature over Sunday, and then heated on the water-bath for a working day (eight hours). This treatment converted it completely into phthalanil.

The second experiment, illustrating the same point, is as follows:—Phthalanilic acid, 3 grms., was mixed with enough aniline to form a thick paste and heated on a boiling water-bath for two minutes. A portion was removed, washed with cold alcohol, and dried. It melted at about 145°, resolidified, and then melted at about 200°, showing that it was unchanged phthalanilic acid. The alcoholic washings, after being concentrated, deposited phthalanil. The flask having been off the water-bath for thirteen minutes was now re-heated for two minutes and a portion of the product tested. It behaved exactly like the first specimen. The flask having been off the bath for twelve minutes was now again heated for six minutes. The product was phthalanil. Eleven minutes' additional heating produced no further change. It may be mentioned that the solubility of phthalanil in alcohol is altogether too slight for it to have been removed from the product of the reaction by washing at the ordinary temperature, and that it must, therefore, have been formed in the wash liquors. These experiments show that, whereas fifteen hours' heating an the water-bath and one night's standing at the ordinary temperature is not sufficient to convert phthanilic acid into phthalanil in the absence of excess of aniline, yet in the presence of such an excess the change is complete after ten minutes' heating and twenty-three minutes' standing.

The phthalanilide which we required was finally prepared from aniline and phthalyl chloride, according to the method of Rogrow (*Ber.*, 1897, xxx., 1442). After re-crystallisation from alcohol it melted at 232—233°, the temperature given in the literature being 231°.

The phthalyl chloride was obtained essentially according to the method of Claus and Hoch (*Ber.*, 1886, xix., 1187),

and of Graebe (*Liebig's Ann. Chem.*, 1887, ccxxxviii., 329). Phthalic anhydride, 50 grms. = 1 mol., was mixed with powdered phosphorus pentachloride, 70 grms. = 1 mol., and heated in a reflux apparatus at 120—170°, during eight hours. Inadvertently, the temperature was allowed to rise for a short time to 210°. The phosphorus oxychloride was volatilised under the ordinary pressure and the residue distilled; it boiled at about 47° (130 mm.). After standing for an hour the distillate deposited crystals which were proved to consist of unchanged phthalic anhydride; they were removed by filtration and the liquid chloride gradually added to an alcoholic solution of aniline, in the manner indicated above. The yield of purified chloride was 22·6 grms. and about 22 grms. of unchanged phthalic anhydride were recovered. The above experimental conditions offer the great advantage of yielding a product which is apparently entirely free from chlorine substitution products isomeric with phthalyl chloride, and from phthalyl tetrachloride. These substances were encountered by the chemists mentioned above, and their separation caused a good deal of trouble and loss of material. We attribute our success chiefly to the distillation of the crude material under reduced pressure, and believe that the yield of phthalyl chloride could be improved by the use of a larger proportion of phosphorus pentachloride, without much danger of the formation of isomeric chlorine compounds. The work is being continued by one of us in conjunction with Mr. Lovelace.—*American Chemical Journal*, xxxvii., No. 6.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1907.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

(Concluded from p. 10).

139. "*The Oxidation of Hydrazines by Free Oxygen.*" By FREDERICK DANIEL CHATTAWAY.

Hydrazines of the formula $R{\cdot}NH{\cdot}NH_2$, where R is a cyclic group, are readily oxidised by free oxygen, the action being accelerated in a remarkable way by alkali hydroxides. In the case of phenylhydrazine dissolved in about three times its weight of 4N-alcoholic potash, oxidation is so rapid that the liquid effervesces freely from escape of nitrogen on mere exposure to the air.

The action appears to be a general one, and results in the liberation of nitrogen and the replacement of the $NH{\cdot}NH_2$ group by hydrogen, thus: $R{\cdot}NH{\cdot}NH_2 + O = R{\cdot}H + N_2 + H_2O$.

It is simply explained by assuming that when such a hydrazine is oxidised, an unstable hydroxyhydrazine is first produced, which at once decomposes, thus:— $R{\cdot}HN{\cdot}NH_2 \rightarrow R{\cdot}HN{\cdot}NH{\cdot}OH \rightarrow RH + N_2 + H_2O$.

The action which takes place in the oxidation of hydrazines is thus closely connected with those reactions of diazonium compounds in which the diazonium group is replaced by hydrogen.

140. "*Calmatambin: a New Glucoside.*" By FRANK LEE PYMAN.

The author described the isolation of a new glucoside, *Calmatambin*, from the bark of a tree indigenous to West Africa, which is known to the natives as *Calmatamba*, and is probably identical with *Canthium glabrifolium*.

The glucoside has the formula $C_{19}H_{28}O_{13},2H_2O$, and crystallises in needles melting at 100°. The anhydrous substance melts at 144—145°. It contains one methoxyl group, has $[\alpha]_D$ - 130·4°, and occurs in the bark to the amount of 1·1 per cent. It is readily hydrolysed by dilute acids and by emulsin.

Octa-acetyl-calmatambin, $C_{19}H_{20}O_{13}(C_2H_3O)_8$, forms needles melting at 179—180°, and has $[\alpha]_D$ - 107·1°.

Calmatambetin, $C_{13}H_{18}O_8,\frac{1}{2}H_2O$, is formed together with dextrose by the action of emulsin on calmatambin according to the equation $C_{19}H_{28}O_{13} + H_2O = C_6H_{12}O_6 + C_{13}H_{18}O_8$. It crystallises in needles melting at 148—149°. It contains one methoxyl group, and is optically inactive. It is readily decomposed by the action of dilute acids, and yields a small amount of a scarlet crystalline *substance*, $C_{11}H_{12}O_3$, melting at 91°, which is volatile with steam, and has an aromatic odour; it may very possibly be a quinone.

The foregoing results show that calmatambin is a β-glucoside, having the constitution represented by the formula $CH_3{\cdot}O{\cdot}C_{12}H_{10}O_2(OH)_4{\cdot}O{\cdot}C_6H_{11}O_5$.

Calmatambin is devoid of any appreciable physiological action.

141. "*The Decomposition of Hyponitrous Acid in presence of Mineral Acids.*" By PRAFULLA CHANDRA RAY and ATUL CHANDRA GANGULI.

Hyponitrous acid, when liberated from silver or mercurous hyponitrite by the action of dilute nitric, hydrochloric, or sulphuric acid at 25° or a higher temperature, decomposes at once according to the following equations:— (1) $2HNO = H_2O + N_2O$; (2) $5HNO = 2H_2O + HNO_3 + 4N$.

Neither nitrous acid, ammonia, or hydroxylamine is formed. The presence of the mineral acids has a specific directive influence in determining the course of reaction.

142. "*The Chemical Composition of Petroleum from Borneo.*" By HUMPHREY OWEN JONES and HUBERT ARTHUR WOOTTON.

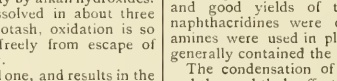
The petroleum from Borneo has been found to consist of approximately equal quantities of homologous hydrocarbons of the paraffin, *cyclo*hexane, and aromatic series, and to contain the members of the naphthalene series to the extent of about 6 to 7 per cent. The less volatile portions of the oil are optically active.

It forms a very convenient source of the nitro- and amino-derivatives of the aromatic hydrocarbons, which may be obtained in large quantities and in a highly pure state.

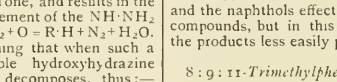
143. "*The Synthesis of Phenonaphthacridines: Trimethylphenonaphthacridines.*" By ALFRED SENIER and PERCY CORLETT AUSTIN.

The authors have employed the methylene di-iodide and arylamine method (Senier and Goodwin, *Trans.*, 1902, lxxxi., 280) for the synthesis of phenonaphthacridines by using equimolecular mixtures of ψ-cumidine and naphthols, and good yields of the two desired trimethylphenonaphthacridines were obtained. When the naphthylamines were used in place of the naphthols, the product generally contained the corresponding dinaphthacridine.

The condensation of trioxymethylene with ψ-cumidine and the naphthols effected the synthesis of the same two compounds, but in this case the yields were smaller and the products less easily purified.

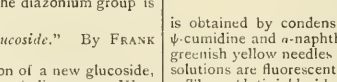


8 : 9 : 11-*Trimethylpheno-* -*naphthacridine*,—



is obtained by condensation of methylene di-iodide with ψ-cumidine and α-naphthol. It crystallises from alcohol in greenish yellow needles melting at 160° (162·5° corr.); its solutions are fluorescent.

The *platinichloride*, *aurichloride*, *mercurichloride*, *picrate*, and *bistrimethylphenonaphthacridine hexabromide* were described.



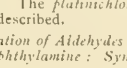
8 : 9 : 11-*Trimethylpheno-* -*naphthacridine*, isomeric

with the above, was obtained in a similar manner, using β-naphthol instead of α naphthol. It crystallises from alcohol in straw-coloured needles, melting at 136° (137° corr.), and its solutions are very faintly fluorescent.

The *hydriodide*, crystallising from aniline in orange

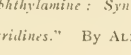
needles, appeared as an intermediate product in the preparation of the base. The *platinichloride*, *aurichloride*, and *picrate* were also described.

144. "*The Condensation of Aldehydes with Mixtures of α-naphthol and α-Naphthylamine: Synthesis of 7-Aryl-*

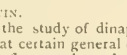


-dinaphthacridines." By ALFRED SENIER and PERCY CORLETT AUSTIN.

In continuation of the study of dinaphthacridines, the authors have found that certain general differences, which they ascribe to steric influence, dependent on the position of the angular rings (compare Hinsberg, *Ber.*, 1902, xxxvi., 4051) between the bases of the type

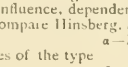


and those of the type

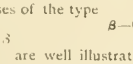


are well illustrated by a detailed investigation of the aldehyde, naphthol, and naphthylamine method of synthesis, first introduced by Ullmann and Fetvadjian (*Ber.*, 1903, xxxvi., 1027).

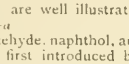
Trioxymethylene does not yield the



dinaphthacridine, whereas it readily forms the

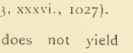


isomeride; benzaldehyde gives the 7-phenyl derivative of both types, and from *m*-nitrobenzaldehyde was obtained



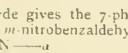
7-*m*-nitrophenyl-dinaphthacridine, whereas Haase (*Ber.*, 1903, xxxvi., 593) found that with β-naphthol and β-naphthylamine it gave a dihydro-derivative of the corresponding dinaphthacridine, which could not be oxidised to the base.

From anisaldehyde and the three tolualdehydes, only derivatives of the

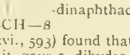


-type could be obtained. It was also noticed that in the preparation of dinaphthacridines of this type, hydro-derivatives were never formed.

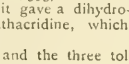
7-*o*-*Tolyl*-*dinaphthacridine* is obtained in yellow crystals melting at 212° (215° corr.), and forms a *platinichloride*, *aurichloride*, and *picrate*.



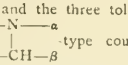
7-*m*-*Tolyl*-*dinaphthacridine* is a yellow crystalline powder melting at 251° (257° corr.), and gives a *platinichloride*, *aurichloride*, and *picrate*.



7-*p*-*Tolyl*-*dinaphthacridine* forms pale greenish yellow rhombohedral crystals melting at 221° (224° corr.), and gives a *platinichloride*, *aurichloride*, and *picrate*.



7-*p*-*Methoxyphenyl*-*dinaphthacridine* crystallises from benzene in small yellow rhombohedra melting at 257° (263° corr.), and forms a *platinichloride*, *aurichloride*, and *picrate*.



7-*m*-*Nitrophenyl*-*dinaphthacridine* crystallises from benzene in small yellow crystals which did not melt below 300°; no sign of fluorescence was observed in any of its solutions. The *platinichloride*, *aurichloride*, and *picrate* were prepared.

145. "*An Improved Form of Apparatus for the Rapid Estimation of Sulphates and Salts of Barium.*" By WILLIAM ROBERT LANG and THOMAS B. ALLEN.

N. Tarugi and G. Bianchi (*Gazetta*, 1906, xxxvi., [i.], 347) have described an apparatus for the rapid estimation of sulphates and salts of barium by a volumetric method based on the rapid clearing of turbid solutions in tubes of narrow calibre. Their apparatus is somewhat complicated, and the authors have simplified it materially. The solution containing the precipitated barium sulphate is forced, by air pressure applied by hand, up a narrow tube, allowed to clear—which it does rapidly as the end-point of the reaction is approached—and a drop of the precipitant added. Any milkiness is plainly observed in the narrow tube, and the solution is washed down into the flask and fresh portions forced up the tube from time to time until further addition of the reagent causes no change. Experiments were made with solutions of sulphuric acid of various concentrations, with the sulphates of copper and of nickel, and also with iron pyrites to determine its sulphur content. The errors as compared with the gravimetric estimation of sulphur as barium sulphate, range from 1 to 0·1 per cent, but such errors are materially reduced by taking the average of five or six titrations, and the whole operation can be completed in less than an hour.

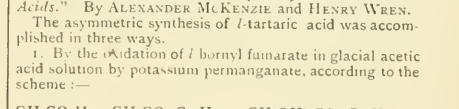
146. "*The Determination of Sugar by Fehling's Solution.*" By WILLIAM ROBERT LANG and THOMAS B. ALLEN.

The apparatus described by the authors (preceding paper) for the estimation of sulphuric acid and sulphates, based on the principle of the rapid clearing of turbid solutions in tubes of narrow calibre, was employed for the determination of dextrose by means of Fehling's solution. Accurate results were obtained when the solution was heated to its boiling-point, the concentration being not more than 0·15 grm. in 75 to 100 cc. of water, and the time of heating being five minutes. Under these conditions the average error varied from 0·1 to 0·30 per cent, but when the solutions were greatly diluted or the time of heating extended from ten to twenty minutes the results varied more than 1 per cent.

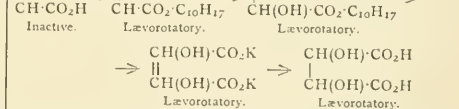
147. "*Studies in Asymmetric Synthesis. VI. The Asymmetric Synthesis of the Optically Active Tartaric Acids.*" By ALEXANDER MCKENZIE and HENRY WREN.

The asymmetric synthesis of *l*-tartaric acid was accomplished in three ways.

1. By the oxidation of *l* bornyl fumarate in glacial acetic acid solution by potassium permanganate, according to the scheme:—



2. By the oxidation of the potassium salt of *l*-bornyl hydrogen fumarate in aqueous solution by potassium permanganate, thus:—



In these two cases the change $\begin{matrix}CH\cdot CO_2H\\ \|\\ CH\cdot CO_2H\end{matrix}$ (inactive) $\rightarrow$ $\begin{matrix}CH(OH)\cdot CO_2H\\ |\\ CH(OH)\cdot CO_2H\end{matrix}$ (active) is rendered possible by the introduction and subsequent complete elimination of the *l*-bornyl group.

3. By the oxidation of *l*-menthyl fumarate in an analogous manner.

The asymmetric synthesis of *d*-tartaric acid was accomplished by the oxidation of the potassium salt of *d*-bornyl hydrogen fumarate, thus :—

$$\begin{matrix}CH\cdot CO_2H\\ \|\\ CH\cdot CO_2H\\ \text{Inactive.}\end{matrix} \rightarrow \begin{matrix}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2H\\ \text{Dextrorotatory.}\end{matrix} \rightarrow \begin{matrix}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2K\\ \text{Dextrorotatory.}\end{matrix} \rightarrow \begin{matrix}CH(OH)\cdot CO_2\cdot C_{10}H_{17}\\ |\\ CH(OH)\cdot CO_2K\\ \text{Dextrorotatory.}\end{matrix} \rightarrow \begin{matrix}CH(OH)\cdot CO_2K\\ |\\ CH(OH)\cdot CO_2K\\ \text{Dextrorotatory.}\end{matrix} \rightarrow \begin{matrix}CH(OH)\cdot CO_2H\\ |\\ CH(OH)\cdot CO_2H\\ \text{Dextrorotatory.}\end{matrix}.$$

148. "*Some Derivatives of 2-Phenyl-1 : 3-naphthylenediamine.*" (Part I.). By Norman Lees and Jocelyn Field Thorpe.

The β-amino-group in 2-phenyl-1 : 3-naphthylenediamine is more strongly basic than the amino-group in the α-position, and is the one first acted on in salt formation, diazotisation, and acetylation. Derivatives of the base, in the formation of which the β-amino-group takes part, can therefore be prepared directly from the base itself, whereas, since the β-amino-group can be readily protected by acetylation, those compounds which are derived from the amino-group in the α-position can be prepared from the monoacetyl derivative of the base.

2-Phenyl-1 : 3-naphthylenediamine combines with diazonium salts, forming azo-compounds, the azo-group entering in the position 4 in the naphthalene ring. The colours of these compounds do not differ appreciably in shade from those of the corresponding compounds derived from 1 : 3-naphthylenediamine; hence the presence of the phenyl group has little or no effect on the colour of compounds of this type.

Typical derivatives of the base have been prepared and investigated. The conditions have also been determined under which it is converted into the corresponding dinaphthol and the two amino-naphthols.

NOTICES OF BOOKS.

Systematic Practical Organic Chemistry. By G. M. Norman, B.Sc., A.R.C.Sc., F.C.S. London: University Tutorial Press, Ltd. 1907.

Candidates for the Board of Education Examination in Practical Organic Chemistry, Stages I. and II., will do well to get a copy of this book, which has been written specially for them. It will be found a great convenience to have all the practical work required in one volume, so that the use of larger works can be altogether avoided, and the little book has merits which will possibly recommend it to others than those for whom it is intended. It gives clear directions for the preparation of most of the important compounds which are considered in an elementary lecture course on organic chemistry, and in most cases mentions the yield that should be obtained when the given quantities of reagents are employed. The chief reactions and properties of the substances prepared are also enumerated, and a scheme of analysis is given for the detection of any of the simple substances, either in a pure state or in aqueous solution, mentioned in the Board of Education syllabus, besides the outlines of a method of determining the class to which a substances belongs without identifying it. The book, which contains some of the recent examination papers, is well arranged, and the student who has conscientiously worked through it should have nothing to fear from his examination.

Photochemie und Beschreibung der Photographischen Chemikalien. ("Photochemistry and the Description of Photographic Chemicals"). By H. W. Vogel. Fifth Edition. By Dr. Ernst Konig. Berlin: Gustav Schmidt. 1906.

The revision of Vogel's standard work by Dr. Ernst König, who is himself a well-known worker, more especially in the region of colour photography, has been a task of considerable magnitude, for it is sixteen years since the last edition was published. The new edition has been considerably abridged in some places, but the pages on optical sensitising, in which Vogel's important discoveries are described, have been left untouched as far as possible. This volume, which is the first part of the Handbuch der Photographie, is divided into three sections. The first gives a short account of the physical effects of light, and the second discusses at some length its chemical action, while the third and last describes the properties and uses of all kinds of photographic chemicals. Dr. König has very wisely not included methods of analysis of these chemicals, regarding such analysis as a question for chemist alone, and not coming into the province of the photographer. The work has long been known as a standard authority on all questions connected with photography, and the latest edition will be heartily welcomed by professionals and amateurs alike.

Catalogue of Bacteriological Apparatus sold by A. Gallenkamp and Co., Ltd., 19 and 21, Sun Street, Finsbury Square, London. 1907.

This illustrated catalogue of bacteriological apparatus includes price lists of all the ordinary apparatus required by Medical Schools, Hospitals, and Medical Officers of Health, as well as for the equipment as regards the analysis of milk, water, foods, &c., of the laboratories of Public Analysts. All kinds of sterilisers, microscopes, microtomes, polarimeters, &c., are fully illustrated, and in the cases of some of the newer or more complicated contrivances directions are given for their adjustment and use.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 9, 1907.

New Reaction to Detect Traces of Moisture.—Wilhelm Biltz.—Potassium lead iodide in contact with water is partly decomposed, yielding yellow lead iodide. To use this properly to test for the presence of water a warm solution of lead nitrate is mixed with a warm solution of potassium iodide. A yellow precipitate is first formed, and disappears on cooling, when a mass of white needles consisting of the double compound is formed. This is dissolved in acetone and filtered, and the solution can either be used as such, or else it can be precipitated with ether, and the amorphous precipitate thus obtained washed with ether and dried in a vacuum desiccator. The salt turns a

pale yellow when kept. A 20 per cent solution of the salt in acetone can be used to detect traces of moisture, a filter-paper on which it is poured turning yellow in a short time. The vapour tension corresponding to 78 per cent sulphuric acid at a temperature of 18°, which is 0·3 mm., can readily be detected. By means of a dry filter-paper impregnated with the solution the presence of water in organic liquids can be detected, or the solid substance can be used for the same purpose.

Chemical Equilibria in the Reactions between Lead Sulphide and its Oxidation Products. — Rudolf Schenck and W. Rassbach.—When the roasting process is applied to lead the following reactions are supposed to occur: $PbS + PbSO_4 = 2Pb + 2SO_2$, $PbS + 2PbO = 3Pb + SO_2$, but the conditions of these apparently simple transformations are not thoroughly understood. The authors have examined the processes to see if equilibrium ensues between the various substances formed. The components of the system are Pb, S, and O, and the possible phases Pb, PbS, $PbSO_4$, PbO (liquid or solid), and SO_2 (gaseous). In order that at any given temperature a definite SO_2 tension may be obtained which corresponds to a state of equilibrium, the presence of three solid or liquid phases is necessary. The heating of three phases to constant temperature must give a definite SO_2 reaction pressure which only depends on temperature. As four liquid or solid substances are present the following combinations are possible :— Pb, PbS, $PbSO_4$; Pb, PbS, PbO ; PbS, $PbSO_4$, PbO ; Pb, $PbSO_4$, PbO. These four combinations would correspond to the four equilibria :—

1. $PbS + PbSO_4 \rightleftharpoons 2Pb + 2SO_2$.
2. $PbS + 2PbO \rightleftharpoons 3Pb + SO_2$.
3. $PbS + 3PbSO_4 \rightleftharpoons 4PbO + 4SO_2$.
4. $Pb + PbSO_4 \rightleftharpoons 2PbO + SO_2$.

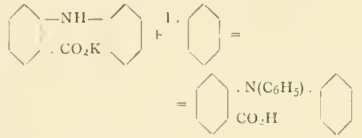
The experimental investigation of these possible equilibria shows that it is only in the first and second systems that equilibrium pressures can be observed.

Sulphation in presence of Mercury.—Otto Dimroth and W. v. Schmaedel.—A patent has recently been taken out by the Badischen Anilin und Sodafabrik for a process in which anthraquinone in sulphuric acid solution is oxidised to amino acids by nitrous acid in presence of mercury. The authors have studied the mechanism of this process, using benzoic acid in place of anthraquinone, and find that not only is the sulphation much accelerated by the presence of mercury, but also *o*-sulphobenzoic acid is produced, as well as the *m*- and *p*-compounds. Only a relatively small fraction of the benzoic acid (*i.e.*, 5 to 7·5 per cent) is sulphated in the ortho-position, and apparently two reactions occur simultaneously. In one part of the benzoic acid the hydrogen is directly replaced by the sulpho-group, giving *m*- and *p*-compounds; at the same time, the benzoic acid reacts with the mercuric sulphate, giving *o* sulphato mercuric benzoic acid, $1-2C_6H_4(CO_2H).Hg.SO_4H$, which with sulphuric acid regenerates mercuric sulphate and yields ortho-sulphobenzoic acid :—

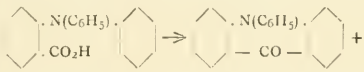
$$C_6H_4(CO_2H).Hg.SO_4H + H_2SO_4 = -C_6H_4(CO_2H).SO_3H + HgSO_4 + H_2O.$$

When anthraquinone is sulphated the indirect action takes place much more quickly than the direct, and hence *a*-anthraquinone sulpho-acid is produced in excess, while the reverse is the case with benzoic acid, and therefore the ortho-compound is produced in relatively smaller quantity.

Triphenylamine and Triphenylamine Carboxylic Acid.—Irma Goldberg and Marie Nimerovsky.—Anthranilic acid can be phenylated with bromo-benzene in presence of copper, but the phenylanthranilic acid thus obtained cannot be further phenylated by the same method. If, however, iodo-benzene is used instead of the bromine compound, diphenylanthranilic acid, or triphenylamino-*o*-carboxylic acid, is readily obtained.



This method is general, and can be carried out with various derivatives of the two components. The triphenylamine-*o*-carboxylic acid thus obtained, when treated with concentrated sulphuric acid, yields N-phenyl acridon,—



and when heated above its melting-point it is converted quantitatively into triphenylamine, carbon dioxide being split off: $(C_6H_5)_2N.C_6H_4.CO_2H \rightarrow N(C_6H_5)_3$. The authors have also found that diphenylamine with iodo-benzene in presence of potassium carbonate and with copper as catalyser can be phenylated, giving pure triphenylamine :—

$$2C_6H_5.NH.C_6H_5 + 2C_6H_5I + K_2CO_3 = = 2(C_6H_5)_3N + 2KI + H_2O + CO_2.$$

Phosphorus Nitride.—Alfred Stock and Hans Grüneberg.—To prepare pure phosphorus nitride the authors used phosphorus pentasulphide and ammonia. The latter they obtained in a pure dry condition by distilling it from commercial ammonia and drying by means of caustic alkali. In order to make phosphorus nitride, the ammonia need not act upon the pentasulphide in the cold, but it is sufficient if the latter is saturated with ammonia at the ordinary temperature. When the complicated mixture of ammonium thiophosphates thus prepared is heated, P_3N_5 is obtained. It is best to heat in a current of ammonia, and all the phosphorus of the original pentasulphide is readily converted into the nitride ; in fact, no other nitride can be prepared so easily in a pure state. The density of P_3N_5 at 18° is 2·51. Its colour varies from pure white to fairly dark reddish brown. The dark coloration is produced when it is heated for some time to temperatures above 850°, and the authors thought that it must be due to the presence of some free red phosphorus. However, when a dark preparation was allowed to cool quite slowly from 900° to the temperature of the room in an absolute vacuum, the colour did not disappear, although free phosphorus would certainly have evaporated. At the ordinary temperature P_3N_5 is very indifferent. It does not redden litmus-paper unless it is heated for some time with water to 100°. When warmed *in vacuo* it begins to decompose into phosphorus and nitrogen at 760°. The nitride may also be prepared in an impure state by heating a mixture of phosphorus pentasulphide and ammonium chloride, and small quantities of it remain when the reaction products of yellow phosphorus or solid phosphine with liquid ammonia are heated to a sufficiently high temperature.

Beryllium Chromate.—B. Glassmann.—To synthesise neutral beryllium chromate chromic acid was neutralised with beryllium carbonate in warm concentrated aqueous solution, and the solution thus obtained was evaporated to crystallisation. The crystals were drained from mother-liquor and dried at 100°. The chromic acid in them was then determined by precipitation as mercuric chromate from dilute nitric acid solution, and the beryllium determined in the usual way in the filtrate, after precipitation of the mercury as mercurous chloride. The formula was thus found to be $BeCrO_4.H_2O$. The reddish yellow

monoclinic crystals of $BeCrO_4.H_2O$ are completely decomposed by water, giving a yellow basic chromate. Basic beryllium chromate, which may also be prepared by precipitating a beryllium sulphate solution with ammonium chromate, is a yellow powder, insoluble in water, and having the composition $BeCrO_4.6Be(OH)_2$ when dried at 100°. The equation representing the decomposition of the neutral chromate with water is $7BeCrO_4.H_2O + 5H_2O = BeCrO_4.6Be(OH)_2. + 6H_2CrO_4$. When excess of chromic acid is added the basic salt again dissolves. The author has not succeded in preparing any acid chromates. Neutral beryllium chromate is completely analogous to magnesium chromate, dried at 100°, $MgCrO_4.H_2O$.

Thorium-cerium Mixtures.—R. J. Meyer and A. Anschütz.—An incandescent mantle of pure thorium oxide is not luminous because it is perfectly transparent to almost all wave-lengths; the addition of a coloured substance, such as cerium dioxide, produces the characteristic luminous effect. The maximum of radiation when 1 per cent of cerium dioxide is present represents the upper limit at which the increase in the power of emission caused by the increase in the amount of cerium is not appreciably affected by the disturbing influence of the ultra red emission. Regarding the question from a chemical point of view, if such oxide mixtures are solid solutions in which the component present in excess, ThO_2, represents the solvent and the other the solute, it remains to be decided between what limits the two oxides are homogeneously miscible with one another, and whether chemical individuals are formed. These questions would easily be answered if it were possible to determine the melting-points of mixtures of different composition, which, however, is not feasible. There is also the question whether in such mixtures the cerium is actually present as dioxide and not wholly or partly as sesquioxide. To investigate this point the authors first tried to ascertain whether any oxygen escapes when ThO_2 and CeO_2 solutions are evaporated together, and obtained a negative result. However, the method employed was open to objection, and hence the active oxygen in the synthetic oxygen mixture was determined iodometrically. It was then found that only a certain part of the cerium used reacts with hydriodic acid, liberating iodine, and thus some of the cerium has been brought into the passive state, *i.e.*, some of the CeO_2 suffers a change, and loses its oxidising properties. Further experiments show that homogeneous solutions of CeO_2 in ThO_2 can be prepared up to a maximum of 7 per cent of CeO_2, but it is not certain whether this maximum percentage represents a compound of 93 per cent of ThO_2 and 7 per cent of CeO_2, which would have the formula $9ThO_2.CeO_2$. It is possible that the maximum effect is produced when 1 per cent CeO_2 is present, because the emission of light does not proceed from the whole mass of dissolved cerium, but from the dissociated parts, and that the maximum of effect corresponds to that dilution at which the solution is completely dissociated.

Products of the Action of Acetanhydride on Phthalamide.—A. Braun and J. Tcherniac.—The principal product of the reaction of acetanhydride upon phthalamide is *o*-cyanbenzamide, $C_6H_4(CO.NH_2)_2 - H_2O = C_6H_4(CN).CO.NH_2$, which is identical with Posner's *o*-cyanbenzaldoxime. When *o*-cyanbenzamide is fused (melting-point 172—173°) it passes into an isomeric substance with a higher melting-point, and the same substance is produced by the action of caustic alkali or ammonia. This isomeric compound is imidophthalamide or phthalimimide, $C_6H_4 < \begin{matrix} CN \\ CO.(NH)H \end{matrix} \rightarrow C_6H_4 < \begin{matrix} C(NH) \\ CO \end{matrix} > NH$, which gives an oxymethyl derivative with formaldehyde and a chlorimide with alkaline hypochlorite. In these reactions it is exactly analogous to phthalimide. With neutral hypochlorite the chief product of the reaction is *o*-cyanbenzoic acid.

Two New Terpenes.—Ossian Aschan.—When the liquid hydrochloride obtained by saturating raw pinene with hydrochloric acid is decomposed with bases at a high temperature and fractionated, between 145° and 150° a new terpene goes over. Its boiling-point is 145—148°, $d_{20/40} = 0{\cdot}8599$; molecular refraction = 43·20; $[\alpha]_D = +1{\cdot}63°$. These constants show that it is a bicyclic hydrocarbon with a double bond, and the author has given it the name pinolene. When its hydrochloride is subjected to the action of aniline another new terpene is obtained, which in its physical constants is closely allied to pinene, and which the author calls isopinene. These two terpenes are now being subjected to an exhaustive examination on a large scale. They appear to belong to the same series of bicyclic hydrocarbons as fenchene, camphene, and bornylene.

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2486.

THE IGNITION POINT OF SULPHUR.

By R. H. McCREA and A. WILSON

The reprint of a paper by Mr. Rutherford Hill on the "Igniting Point of Sulphur" appeared in the Chemical News (vol. xcv., p. 169). In this paper there is a brief *résumé* of the work done on the above subject, and it appeared from it that some results had been obtained which were irreconcilable with the author's own, who had obtained the lowest point, viz., 248° C. Since then we have worked at the subject ourselves with regard to the ignition of sulphur both in air and oxygen.

We had not access to the author's previous paper in which the apparatus he used is described, so we had to evolve our own method. After various unsatisfactory results with air and paraffin baths the following method was adopted:—A small amount of sulphur—about a grm.—was placed in the bend of a U-tube of 10 mm. diameter, which was immersed in a sulphuric acid bath. One limb of this tube was connected with a water-pump, and the other, through which the aspirated air entered, was connected with a spiral of glass tubing, bent in the form of a "worm," also immersed in the sulphuric acid bath. As the question of pressure entered, a mercury manometer was connected by means of a three-way tube close to the exit limb of the U-tube. This spiral was discarded after several trials, as it did not appear to modify the results. When air was slowly aspirated through the apparatus, the manometer indicating a decrease of 2 mm. pressure, the ignition point was fairly high; but it was found by increasing the current of air till 6 mm. was registered, that the ignition point was lowered, while further increase in this direction had the reverse effect, probably through chilling. As the temperature of the sulphur naturally lagged behind that of the bath, the latter was brought slowly to the temperature required, and was maintained at this point for about five minutes, while the air was allowed to stream slowly through. When the temperature had been constant for some time the current was increased as above. It was found that for temperatures below 255° C. (uncorrected), the sulphur refused to ignite, but above this ignition easily took place. Four nearly consecutive results were obtained in this way for 255° C. (uncorrected for exposed stem).

For oxygen our results are anomalous. The following method was adopted: — Oxygen from one of Brin's cylinders was allowed to stream over the sulphur, in this case the manometer being fixed near the inlet limb. Low results were not obtained when the current of gas was passing, and the lowest results were got as follows:—Oxygen was blown through the tubes to displace the air, and was then allowed to stream through slowly while the bath was maintained at constant temperature. The current was increased for a few moments and then quickly shut off, the pressure falling to atmospheric, and ignition occurring then if the temperature was sufficiently high. The concordant results in the case of air were not obtained here, the following being the lowest:—257°, 259·5°, 259·5°, 263·5°, 264° C. (uncorrected).

As to the question of SO_2 being formed below the ignition point our results give an affirmative answer. The oxygen issuing from the apparatus was passed through a very weak solution of potassium permanganate and decolorised this; the liquid also smelt strongly of sulphur dioxide. Ten cc. of the permanganate solution were placed in a test-tube and the issuing gas (oxygen) bubbled through at the rate of one and a-half bubbles per second, at three different temperatures, under the same conditions.

At 160°	decolorisation	took place	in	65	minutes.
At 200°	„	„	„	6·5	„
At 250°	„	„	„	3	„

(Temperatures uncorrected; permanganate about one-twentieth decinormal).

We agree with Mr. Hill that the details of apparatus may make a difference in the results obtained. We would also point out that if a thermometer is used to measure fairly high temperatures over any period it cannot be relied on. In subsequently standardising ours we found its indications in error by several degrees. We do not say that we have obtained the lowest point possible, nor do we try to explain the fact that we got a higher result with oxygen than with air. The results were undoubtedly got at a higher pressure, but the atmospheric pressure itself varies through far greater limits than this, and we have not noticed it mentioned in the other determinations. At the time of the air experiments the barometer stood at 763 mm., and in the case of oxygen at 760 mm. We would suggest that, under the conditions of the experiment, the concentration of the oxygen in the air, measured by its partial pressure, was sufficient to oxidise all the sulphur vapour formed at the temperature of ignition, measured by its vapour tension. Thus, an increase in the concentration of the oxygen—when the latter alone was used—might not lower the ignition point, the specific heat of oxygen being near that of the diluent nitrogen. In the paper referred to, Mr. Hill says that in a recent experiment "when both thermometers indicated 255° C. the sulphur vapour and air ignited," but he does not say whether this figure was read directly or corrected for the exposed part of the stem, if there were any. In the latter case the correction would make probably a considerable difference.

The temperature of ignition in air found by us, the bulb of the thermometer being placed in the bath on a level with the bend of the U-tube, and correction made for the exposed part of the stem, was 261° C.

Herne Bay, July 6th, 1907.

CONTRIBUTIONS TO THE CHEMISTRY OF GOLD.*

By F. H. CAMPBELL, M.Sc. (Melbourne).

(Concluded from p. 17).

Preparation of Aurous Oxide, Aurous Nitrate, and the Determination of the Normal Potential of Au· Ions.

Various methods for the preparation of Au_2O were tested. Treatment of AuCl with dilute KOH was found to be unsatisfactory, the yield being exceedingly small owing to the formation of a complex salt; further, the precipitate obtained was so fine that it was difficult to filter and purify. The precipitate obtained when insufficient $KHCO_3$ is added to a boiling solution of Au in aqua regia should be aurous hydroxide—but in practice, a mixture of Au and a substance soluble in concentrated HNO_3 was obtained. By pouring a solution of Au in aqua regia into a boiling mixture of solutions of NaOH and $Na_2C_2H_2O_2$ a small quantity of an easily washable flocculent black precipitate was obtained. With the object of increasing the yield $NaHCO_3$ was substituted for NaOH with satisfactory results; at the same time the yield was always exceedingly small, and variation in the conditions of precipitation had little or no influence. The details of the method were as follows:—The solutions were mixed when cold, and the addition of the acid solution was stopped while the

* A Paper read before the Faraday Society, May 28, 1907.

$NaHCO_3$ solution was still slightly alkaline. The resulting yellow solution became brown on warming, and at higher temperatures a flocculent light brown precipitate separated. The precipitate was filtered through a Gooch crucible, in the bottom of which was a disc of filter-paper. When free from soluble salts it was dried at 110°, separated from the paper, and treated repeatedly with cold concentrated HNO_3 in order to remove the relatively much more soluble Au_2O_3 which was always present; after a final wash with water the substance was again dried at 110°.

The brown substance so obtained was not analysed; the total amount obtained was so small and the amount required for a satisfactory analysis comparatively so large that it was considered inadvisable to use any of it in this way. That the substance was not merely metallic though containing metallic gold, as will afterwards be shown, was considered to be sufficiently proved by the facts that the colour was darker than that of gold, that it did not show metallic lustre on being rubbed with a pestle, and that it was soluble in HNO_3. In addition to the purely chemical methods of preparation an attempt was made to obtain Au_2O by anodic oxidation. A cell, having a quantity of precipitated gold as the anode and a platinum-wire as cathode, was filled with a moderately concentrated solution of K_2SO_4. A current at 10 volts was passed for some hours. At the end of the experiment it was found that, though no change had taken place at the anode, the cathode had become covered with black spongy gold. Gold was not detectable in the solution.

From the oxide the nitrate solutions were made by shaking excess of Au_2O with solutions of HNO_3 of various concentrations—the acid used was proved to be free from impurities, volatile or non-volatile. Potential measurements were made a week or longer after the solutions had been made.

On account of the smallness of the concentration of the Au_2O solubility determinations were made in the case of the two strongest only. This was done by evaporating a large bulk of the solution to dryness in a weighed porcelain dish and igniting the residue; ignition was necessary because Au_2O is not quickly decomposed at temperatures below 250°. The assumption that we have a solution of $AuNO_3$ is favoured by the fact that the residue, probably pure Au_2O, did not change its black colour for that of Au until strongly heated. It may be mentioned that a few experiments were made with a solution of H_2SO_4, and that when this was evaporated to dryness a white residue (probably Au_2SO_4) was obtained, which became first black (Au_2O) and then red (Au) on being strongly heated. In Table V. are given the results of the solubility determinations.

Table V.

Strength HNO_3.	No. cc. analysed.	Grms. Au found.	Grms. Au per litre.
9·13 N	150	0·0012	0·008
11·66	200	0·0032	0·016
11·66	200	0·0035	0·0175

The action between HNO_3 and Au_2O may be represented by the equation $Au_2O+2HNO_3=2AuNO_3+H_2O$ or $Au_2O+2H^{\cdot}=Au^{\cdot}+H_2O$ (see Note); hence, according to the law of mass action, $\frac{(Au_2O)\,.\,(H^{\cdot})^2}{(H_2O)\,.\,(Au^{\cdot})^2}$ = constant (see Note), the active masses of Au_2O_3 and H_2O are constant, so that the concentration of $Au^{\cdot}$ is directly proportional to that of the $H^{\cdot}$ ions; in other words, if we assume that both $AuNO_3$ and HNO_3 are equally ionised, the concentration of $AuNO_3$ varies directly, as does that of the solvent. (The table does not seem to prove this conclusion, but the error of measuring such small solubilities is too great to form a serious objection). On this assumption the concentration of $Au^{\cdot}$ ions, and hence their normal potential, that is, the potential for normality of $Au^{\cdot}$ ions, have been calculated in the case of those solutions in which no direct concentration estimation was possible (compare Cumming, *Trans. Faraday Soc.*, Feb., 1907, ii., 205).

(Note.—This equation contains even the action of any other acid in aqueous solution on aurous oxide, and explains why aurous fluoride cannot exist, the hydrofluoric acid forming very little $H^{\cdot}$ ions; see Lenher, *Journ. Am. Chem. Soc.*, 1903, xxv., 1136).

The potential measurements were made by means of the compensation method; a sensitive d'Arsonval galvanometer served as Nul instrument. As it was found impossible to obtain satisfactory measurements unless the electrode was in contact with solid Au_2O, a slight modification was made in the ordinary form of electrode vessel; a tube about 2 mm. in length and 1 mm. in diameter was sealed to the bottom of the cell. By these means the short wire electrode could be completely covered by a very small quantity of the solid. The electrodes consisted of platinum-wires, sealed into glass tubes in such a way that about 2 mm. of the wire was left exposed; connection was made by means of a copper-wire joined to the protected end of the platinum. It was found that platinised platinum and gilded electrodes gave the same results, and that these agreed with those obtained when a platinum electrode was used in contact with a mixture of pure Au and Au_2O, prepared as already described. This would serve to show that the Au_2O used has an admixture of metallic gold, which forms the lower oxidation state of the reversible Au_2O electrode. Most of the measurements were made with platinised platinum electrodes.

In Table VI are given the potentials measured, ϵ, and the normal potential, ϵ_0, calculated from them by means of Nernst's formula: $-\epsilon=\epsilon_0+\frac{RT}{n\mathrm{F}}\log_n i$. In the case under consideration the valency $n=1$, so that $\epsilon_0=\epsilon_1-0{\cdot}059\log_{10} i$; i being the concentration of the mols. gold in solution taken as being $Au^{\cdot}$ ions.

Table VI.

HNO_3 normality.	Grm.-mols. of $Au^{\cdot}$ per litre.	ϵ against n calomel electrode.	ϵ against n hydrogen electrode.	ϵ_0
3·32	0·00002 (*a*)	0·835	1·118	1·40
7·76	0·000047 (*a*)	0·901	1·184	1·44
8·77	0·000053 (*a*)	0·923	1·206	1·46
9·13	0·00041	0·932	1·215	1·47
11·66	0·00086	0·998	1·281	1·52
			Mean =	1·46

(*a*) These values were obtained by interpolation from the solubility values given in Table V., on the assumption that $(Au^{\cdot})=0{\cdot}6\ 10{-}5\ (HNO_3)$, as calculated from the average solubility product $0{\cdot}7\ 10{-}19$ of AuOH. This approximation is probably sufficiently accurate for present purposes, as any variation in the value for $Au^{\cdot}$ makes a comparatively small alteration in ϵ_0.

A normal calomel electrode was used as the other half-cell, and the two connected by means of a saturated ammonium nitrate solution, to eliminate, as far as possible, the diffusion potential (Cumming, *Trans. Faraday Soc.*, 1907, ii., 213). The above figures ϵ_0 represent the normal potential of $Au^{\cdot}$ ions compared with the hydrogen standard. Taking the mean, we have as limiting minimum value for the normal potential, $\epsilon_h\mathrm{Au_{metal}}/n\mathrm{Au}^{\cdot}=+1{\cdot}5$ volts above hydrogen standard. The value 1·5 of the $Au^{\cdot}$ potential being considerably above that of oxygen, 1·22, the fact that the aurous compound is very labile and difficult to prepare are easily explicable. In fact, according to these figures the dissociation tension of O_2 from Au_2O is far greater than the atmosphere. From the hydrolysis of $AuNO_3$, *i.e.*, the solubility of Au_2O in HNO_3, we are able to calculate the approximate value of the solubility product $(Au^{\cdot})\,(OH')$ of Au_2O. $(Au^{\cdot})\,(OH')=(Au^{\cdot})\,\frac{1{\cdot}2\times10^{-14}}{(H^{\cdot})}$ assuming $(Au^{\cdot})$ to be the concentration of Au dissolved and $(H^{\cdot})$ that of the HNO_3. Hence we get—

Table VII.

Strength of acid.	Solubility product.
9·13 *n*	$0·52 \times 10^{-19}$
11·66	$0·86 \times 10^{-19}$

The small affinity between gold and iodine, the tendency to form an iodine complex, the high oxidation potential of $Au^{\cdot}$ ions, and the very low solubility product of Au_2O all agree to confirm the assumption that Au forms very weak positive ions.

With respect to the trivalent state, the results show that the same is true. The tendency of aurous compounds to decompose into an auric compound and metallic gold probably indicates that an equilibrium between the two states exists in which the concentration of each is of the same order of magnitude, and hence of approximately the same potential against the metal.

I take this opportunity to express my deepest thanks to Prof. Abegg, by whom the subject of this research was suggested, and to whose continual interest and advice its success is largely due.

RETIREMENT OF PROFESSOR LUNGE.

The news of the approaching retirement of Dr. Georg Lunge from the professorship of Technical Chemistry at Zurich Polytechnic will be received with great regret by all who know of his valuable work as a teacher, in a post which he has held for more than thirty years. His loss will be felt keenly by his students, for to them he has been not only a lecturer whose knowledge of technical chemistry is unequalled, but also a personal friend, who was ever ready to place at their disposal his experience and counsel. Professor Lunge has an extensive circle of friends in England, for he spent some years in this country while acting as manager of large soda works in the Tyne district, a post he gave up only when appointed to the Professorship at Zurich. His "Text Book of the Soda Industry," the first volume of which appeared in 1879, is still the standard book upon the subject, while his "Treatise on the Chemical Examination of Technical Products" is one of the most comprehensive works on analysis extant. His investigations of the lead chamber reactions in the manufacture of sulphuric acid and upon the composition and action of bleaching-powder early made his name known all over Europe as a worker of great skill and ingenuity, while the wideness of his knowledge of technical chemistry may be gauged by calling to mind the text-books upon different branches of technology which came from his pen. It only remains for us to express the hope that he may live many years to enjoy the rest from his arduous professional duties, which latterly imposed too great a strain upon both mind and body, and that he may have sufficient strength to add to the number of valuable books which he has already given to the world.

Alloys of Nickel and Tin.—Em. Vigouroux.—Alloys of nickel and tin, containing from 0 to 40 per cent of the latter, may be prepared by heating a mixture of the two metals in a current of hydrogen in a Schlœsing furnace. Such alloys are feebly magnetic, and yield, when treated with nitric acid and potash, a substance with the formula Ni_3Sn. This substance when powdered is brown in colour; it is non-magnetic and is soluble in nickel. Its density at 0° is 8·98. It is attacked by oxygen at a red heat and by chlorine. Hydrochloric acid acts upon it at ordinary temperatures even when dilute, and completely dissolves it when heated. Sulphuric acid acts more rapidly, and aqua regia more energetically still. Cold dilute nitric acid has but little action, but the hot concentrated acid gives metastannic acid. Potash solution has no action upon it, and fused potash corrodes it only very slowly.—*Comptes Rendus*, cxliv., No. 24.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, July 4th, 1907.

Sir Alexander Pedler, C.I.E., F.R.S., Vice-President, in the Chair.

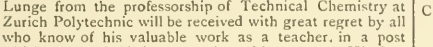
Messrs. M. D. Cowap, H. McCombie, O. E. Elias, and S. F. Stell were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Benjamin Owen Jones, Boksburg, Transvaal; Thomas Callan, B.Sc., 22, Church Street, Egremont, Cheshire; Robert Harry Smith, Apsley House, Priory Road, Sheffield.

Of the following papers, those marked * were read:—

*149. "iso*Nitroso- and Nitro-dimethyldihydroresorcin*." By Paul Haas.

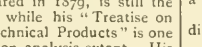
When an ice-cold aqueous solution of the potassium salt of dimethyldihydroresorcin mixed with potassium nitrite is acidified, a pale yellow precipitate of iso*nitrosodimethyldihydroresorcin* (I.)—



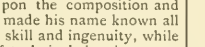
I. II.

is obtained. That this substance is in reality an *iso*nitroso-derivative and not a nitroso-derivative is shown by the fact that it does not give Liebermann's reaction, but on the contrary yields coloured *potassium*, *ammonium*, and *ferrous* salts after the manner of α-oximino-ketones. When *iso*nitrosodimethyldihydroresorcin suspended in ether is saturated with oxides of nitrogen, prepared from nitric acid and arsenious oxide, it is converted into *nitrodimethyldihydroresorcin* (II.); this substance may also be prepared in a similar manner from dimethyldihydroresorcin itself.

The base (III.), obtained by the action of ammonia on dimethyldihydroresorcin (*Trans.*, 1906, lxxxix., 191)—

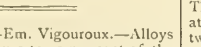


III.



IV.

when suspended in water and treated with nitrous acid at 0°, yields an iso*nitroso*-derivative of the formula (IV.), which gives a crimson *potassium* salt and a blue *ferrous* salt. Both *iso*nitroso- (I.) and nitro-dimethyldihydroresorcin (II.) on reduction yield an amine which is converted by nitrous acid into a substance of the formula $C_8H_{10}O_2N_2$. That nitrous acid in acting on the base (III.) really attacks the carbon atom in the para-position relative to the two methyl groups, and not the imino-group, is shown by the fact that this *iso*nitroso-derivative (IV.) yields on reduction and subsequent treatment with nitrous acid, the same substance, $C_8H_{11}ON_3$, as is obtained by a similar series of reactions from the *mono-oxime* of *iso*nitrosodimethyldihydroresorcin (V.)—



V.

in which the nitrogen atoms are clearly attached to different carbon atoms.

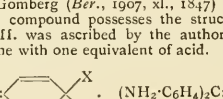
*150. "*The Structure of Carbonium Salts.*" By Frank Baker.

The author has examined the absorption spectra of the sulphates of several derivatives of benzylideneacetone, and

also of triphenyl- and trianisyl-carbinol sulphates. These carbonium salts gave rise to two characteristic types of absorption.

p-Rosaniline base, as well as the mono-hydrochloride, shows the first type of curve, whilst in presence of more concentrated acid the second of these types of spectra is observed. From these results, the author concluded that the magentas are carbonium salts, similar to triphenyl-carbinol sulphate.

Since Gomberg (*Ber.*, 1907, xl., 1847) has shown that the latter compound possesses the structure I., the constitution II. was ascribed by the author to the salts of *p*-rosaniline with one equivalent of acid.



I. II.

The second of the above-mentioned types of curve is similar to those of the hydrochlorides of certain members of the hydroxyazo-group (Tuck, *Trans.*, 1907, xci., 449), and the author suggested that these salts are also carbonium compounds.

The absorption spectrum of triphenylmethane was found to differ from that previously described by Hartley (*Trans.*, 1887, li., 152).

Discussion.

Dr. Cain mentioned that Gomberg himself, in the paper quoted by the author, adopted Nietzki's formula, $(NH_2 \cdot C_6H_4)_2C{:}\langle{=}\rangle NH_2X$, for the salts of *p*-rosaniline.

In view of the work of Hantzsch and Ostwald, and other chemists, which are generally considered to establish the correctness of Nietzki's formula, it was not likely that Mr. Baker's suggestion would be accepted by colour chemists, particularly as it seemed so improbable that the acidic group X should be attached to the carbon and not to the nitrogen atom.

Dr. Hewitt saw no necessity to ascribe a carbonium formula to the salts of hydroxyazo-compounds with mineral acids. Chemical reactions pointed to their substances having a quinonoid structure, but it was the phenolic nucleus which apparently becomes altered.

In reply, Mr. Baker pointed out that Gomberg had suggested that in the formation of magenta from *p*-rosaniline base a carbinol corresponding to the salt of the structure shown by (II.) was first formed, and that this compound passed into the iminoquinone, but no proof of the latter change had been presented.

*151. "*Studies of Dynamic Isomerism.* Part VI. *The Influence of Impurities on the Mutarotation of Nitrocamphor.*" By Thomas Martin Lowry and Egbert Hochey Magson.

The velocity of mutarotation of nitrocamphor has been measured in a number of different solvents and in presence of a variety of added impurities.

In the experiments on glucose described in the first paper of this series (*Trans.*, 1903, lxxxiii., 1314), it was found that the mutarotation in aqueous solutions could not be retarded by the addition of either acid or alkali, and appeared to be due to a direct interaction between the sugar and the solvent. In the case of nitrocamphor dissolved in chloroform, however, it has been found possible to retard the isomeric change by the addition of small quantities of acid, thus confirming the view already arrived at (*Trans.*, 1899, lxxv., 221) that the mutarotation of the nitrocamphor in solvents such as chloroform and benzene is conditioned by the presence of alkaline impurities.

Sodium ethoxide added to an alcoholic solution of nitrocamphor was found to produce an acceleration very similar to that which results from the addition of potassium hydroxide to an aqueous solution of glucose. Extraordinary effects were produced, however, by the addition of piperidine to solutions of nitrocamphor in benzene or chloroform. In presence of N/1000 piperidine no mutarotation could be detected, with N/10,000 piperidine the mutarotation was complete in five minutes, with N/100,000 in an hour, and with N/1,000,000 in about ten hours; with N/10,000,000 piperidine the acceleration was of the same order of magnitude as that due to the trace of impurity normally present in the purified materials.

Discussion.

Mr. W. A. Davis, replying to the question raised by Dr. Lowry as to the origin of the peculiar odour noticed in the chloroform solutions used, suggested that it was due to carbonyl chloride formed by the action of the air on the chloroform. It would appear that this change was accelerated by the presence of an acid, in this case trichloroacetic acid; it was already well known that it could be prevented by having an alkali present, such as lime.

*152. "*The Relation between Absorption Spectra and Chemical Constitution.* Part VIII. *The Phenylhydrazones and Osazones of α-Diketones.*" By Edward Charles Cyril Baly, William Bradshaw Tuck, Effie Gwendoline Marsden, and (in part) Maud Gazdar.

From a consideration of their absorption spectra it was shown that the phenylhydrazones and osazones of the *α*-diketones in neutral solution possess the ketonic constitution, and that in alkaline solution the former tend to favour the enolic configuration, thus:—

Neutral solution.	Alkaline solution.
$R \cdot C{:}N \cdot NH \cdot C_6H_5$	$R \cdot C \cdot N{:}N \cdot C_6H_5$
$\vert$	$\Vert$
$R \cdot CO$	$R \cdot C \cdot OH$

In the phenylhydrazones of hydroxy-ketones in which the hydroxyl group is adjacent to the :C:N· linking, direct evidence is found of the mutual influence of the hydroxyl group and the C:N linking. This influence is best shown in the great retardation of the change of the hydrazone to the azo-form in light; moreover, it is this mutual influence which renders possible the oxidation of the hydroxyl group by excess of phenylhydrazine. Inasmuch as the change to the azo-form removes this influence upon the hydroxyl group, this change tends to restrain the oxidation of the hydroxyl group by phenylhydrazine, and as, further, acetic acid retards the change to the azo-form, so the presence of acetic acid aids the formation of the osazones with excess of phenylhydrazine.

153. "*Permanganic Acid.*" By Matthew Moncrieff Pattison Muir.

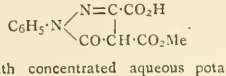
By adding the equivalent quantity of dilute sulphuric acid to a solution of barium permanganate, filtering through glass-wool, and evaporating over sulphuric acid in a vacuum, solutions of permanganic acid, $HMnO_4$, containing about 17 per cent of the acid, can be obtained. A small quantity of a fairly concentrated solution of this acid, when left in an open vessel, deposits brown oxides of manganese ($xMnO_2, yMnO$, where $x=20$ and y varies from 6 to 10), mixed with violet-blue crystals of the acid. The latter could not be obtained as a solid except mixed with oxides of manganese. A very dilute solution of permanganic acid can be boiled without decomposition; a solution containing about 4 per cent of the acid deposits a brown film on glass on keeping for half-an-hour. More concentrated solutions decompose gradually with evolution of ozonised oxygen; when evaporated to dryness over sulphuric acid in a vacuum, they give black, almost pure, manganese dioxide.

154. "*Methyl Dicarboxyaconitate.*" By Siegfried Ruhemann.

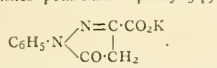
The author has found that the esters of dicarboxyaconitic acid are not produced in a manner similar to the formation of ethyl dicarboxyglutaconate, namely, by the action of the esters of trichloroacetic acid on ethyl sodiomalonate, but methyl dicarboxyaconitate

$CO_2Me{\cdot}C{:}C(CO_2Me)_2{\cdot}CH(CO_2Me)_2$, was prepared according to the directions of Anschütz and Deschaur (*Annalen*, 1906, cccxlvii., 3).

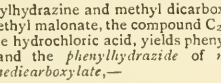
Phenylhydrazine reacts with the ester at the ordinary temperature to yield the *additive* product, $CO_2Me{\cdot}C(NH{\cdot}NH{\cdot}C_6H_5){\cdot}CH(CO_2Me)_2]_2$ (colourless prisms, m. p. 135°). This is fairly stable, but is decomposed when it is digested with dilute caustic potash or boiled with sodium carbonate with formation of malonic acid and *monomethyl phenylpyrazolonedicarboxylate* (colourless prisms which melt and decompose at 201—202°). The author considers that the formula of this ester is—



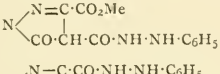
On boiling with concentrated aqueous potassium hydroxide, it furnishes potassium 1-phenyl-5-pyrazolone-3-carboxylate,—



At 100°, phenylhydrazine and methyl dicarboxyaconitate form, besides methyl malonate, the compound $C_{24}H_{24}O_4N_6$. This, with dilute hydrochloric acid, yields phenylhydrazine hydrochloride and the *phenylhydrazide* of *monomethyl phenylpyrazolonedicarboxylate*,—



or—



(colourless needles which decompose on heating).

The compound $C_{24}H_{24}O_4N_6$ therefore is the *phenylhydrazine* salt of this substance.

Methyl dicarboxyaconitate, on being heated with aniline at 100°, is decomposed, and furnishes *carboxymethylanilinomethylenemalonanil*,—

$$CO_2Me{\cdot}C(NH{\cdot}C_6H_5){:}C{<}\begin{matrix}CO\\CO\end{matrix}{>}N{\cdot}C_6H_5$$

(canary-yellow prisms, m. p. 194°).

155. "*The Action of Heat on α-Hydroxycarboxylic Acids.* Part III. *αα'-Dihydroxysebacic Acid and its Diacetyl Derivative*." By Henry Rondel Le Sueur.

The author has now extended his investigation of the action of heat on α-hydroxy-acids to the hydroxy-derivatives of dibasic acids. When αα'-dihydroxysebacic acid or its diacetyl derivative is heated at 250—270°, it decomposes with evolution of carbon monoxide and formation of the dialdehyde of suberic acid :—

$$CO_2H{\cdot}CH(OH){\cdot}[CH_2]_6{\cdot}CH(OH){\cdot}CO_2H \rightarrow \rightarrow CHO{\cdot}[CH_2]_6{\cdot}CHO.$$

156. "*Dihydroxyadipic Acids.*" (Preliminary Note). By Henry Rondel Le Sueur.

When the bromine atoms in αα'-dibromoadipic acid are replaced by hydroxyl groups, two dihydroxyadipic acids are obtained, one melting at 146° and the other at 174°. Both form insoluble crystalline silver salts, and when the acid melting at 146° is heated, it loses water, with formation of a dilactone which sublimes in well-defined plates.

As αα'-dihydroxyadipic acid contains two asymmetric carbon atoms, it is probable that the above acids are stereoisomerides.

157. "*The Relation between Absorption Spectra and Optical Rotatory Power.* Part II. *The Tartaric Acids.*" By Alfred Walter Stewart.

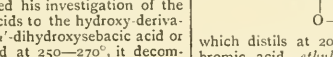
The absorption spectra of the two active forms of tartaric acid are identical, and show only slight general absorption. When an equimolecular mixture of the two antipodes containing the same weight of acid as in the previous cases is used, a greater general absorption is found, proving that racemic acid has a greater power of absorption than either active form. When the racemic acid solution is diluted, however, its absorptive power gradually approximates to that of the active acids, with which it eventually becomes identical. This shows that in dilute solution the racemic acid is broken down into the two active forms, as has already been suspected from results obtained in freezing-point, boiling-point, and vapour density determinations. These spectroscopic results were corroborated by somewhat similar ones obtained with the active limonenes and dipentene. As a double salt above and below its temperature of transition furnishes the closest parallel to a solution which may contain either a mixture of two antipodes or a racemic compound, the spectrum of astrakanite above and below 22° was examined. It was found that above this temperature an absorptive power was shown differing from that observed below 22°, so that the two cases are evidently analogous. This also furnishes a new method of determining transition temperatures. It was found that *i*-tartaric acid had the strongest absorptive power of all, being much more absorbent than racemic acid. No absorption bands were found in any of the spectra. Applications of this work to various questions, such as the determination of existence limits in the case of racemic compounds, the proof of the actual formation of a liquid racemic compound (as distinct from an inactive equimolecular mixture), and the existence of pseudo-racemic compounds were discussed.

158. "*Experiments on the Synthesis of the Terpenes.* Part XI. *Synthesis of 4-Isopropylidenecyclohexanone and its Derivatives.*" By William Henry Perkin, jun., and John Lionel Simonsen.

The sodium derivative of ethyl α-acetylglutarate, $CO_2Et{\cdot}CHNa(COMe)CH_2{\cdot}CH_2{\cdot}CO_2Et$, reacts readily with ethyl β-iodopropionate with the formation of *ethyl γ-acetylpentane-αγε-tricarboxylate*,—

$$CO_2Et{\cdot}C(COMe)(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2,$$

which distils at 217° (15 mm.), and on hydrolysis with hydrochloric acid is converted into *γ-acetylpimelic acid*, $COMe{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2H)_2$. This acid is a colourless syrup which yields a *semicarbazone* melting at 177°. When ethyl γ-acetylpimelate is treated with magnesium methyl iodide, it is converted into the lactone of *ethyl hydrogen γ-isopropenolpimelate*,—

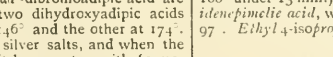


which distils at 200° (22 mm.), and yields, with hydrobromic acid, *ethyl hydrogen γ-(bromoisopropyl)pimelate*, $Me_2CBr{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2Et)CH_2{\cdot}CH_2{\cdot}CO_2H$.

Ethyl γ-(bromoisopropyl)pimelate,—

$$Me_2CBr{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2,$$

obtained by the esterification of the latter compound, is decomposed by pyridine with formation of *ethyl γ-isopropylidenepimelate*, $Me_2C{:}C(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$ (b. p. 168° under 13 mm.), and on hydrolysis, yields *γ-isopropylidenepimelic acid*, which crystallises in prisms and melts at 97°. *Ethyl 4-isopropylidenecyclohexanone-2-carboxylate*,—



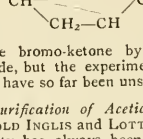
is obtained when the solution of ethyl *γ-isopropylidenepimelate* in toluene is treated with sodium; it decomposes on distillation, combines with hydrogen bromide to form *ethyl-4-β-bromoisopropylcyclohexanone-2-carboxylate*, and is hydrolysed by alcoholic potash with formation of *4-isopropylidenecyclohexanone*,—

$$Me_2C{:}C{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}CO,$$

This ketone distils at 219°—221°, and yields a *semicarbazone* which melts at 201° ; hydrobromic acid converts it into 4-β-*bromoisopropyl*cyclo*hexanone*,—

$$Me_2CBr\cdot CH\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CO.$$

The object of this research was to endeavour to synthesise nopinone,—



from the above bromo-ketone by the elimination of hydrogen bromide, but the experiments which were made in this direction have so far been unsuccessful.

159. "*The Purification of Acetic Ester.*" By JOHN KENNETH HAROLD INGLIS and LOTTIE EMILY KNIGHT.

Great difficulty has always been experienced in preparing pure acetic ester, and although several methods have been suggested, no one of them is satisfactory, since the yield of pure ester is small, and the process of preparing it laborious. For the preparation of aceto-acetic ester, very nearly pure acetic ester is required, and the presence of a moderate quantity of alcohol—the most likely impurity—is fatal to success. A series of experiments has shown that the separation can be most easily carried out by first converting the alcoholi nto an ester of high boiling-point, and then distilling. If the crude ester, as obtained in the ordinary continuous process, is dried over potassium carbonate (which also removes any acetic acid) and treated with phosphoric oxide, a slow action takes place with the formation of phosphoric esters which are neither volatile nor decomposed at the boiling-point of ethyl acetate (77·20° corr.). In this way a yield of 160 grms. of ester boiling within one degree was obtained in an experiment in which the theoretical yield was 264 grms. ; that is 60 per cent of ester was obtained pure.

This process, however, is slow, and requires several days for completion at the ordinary temperature. On the other hand, the removal of the alcohol takes place more rapidly at the boiling-point. Thus, a mixture of 100 grms. of ester (b. p. 76·65—77·15°) with 8 grms. of absolute alcohol distilled continuously between 73° and 77°, only 21 grms. passing over above 76·3°. When, however, the fractions had been mixed together and heated for half-an-hour with 10 grms. of phosphoric oxide, using a reflux condenser, a single distillation gave 72 grms. of distillate between 76·7° and 77·2°; that is, 72 per cent of an approximately pure substance. This result shows that it is easy to obtain by this method a good yield of acetic ester boiling within 0·5°; and it was found that an ester of this purity gave a good yield of acetoacetic ester.

160. "*Solubility of Lead Sulphate in Concentrated Solutions of Ammonium Acetate.*" (Preliminary Note). By JOHN JACOB FOX.

Solubility experiments were carried out with the view of determining the course of the reaction occurring between ammonium acetate and lead sulphate. The solid phases were examined to ascertain whether they changed during the solution. The following are some of the results obtained from the analysis of the solutions saturated at 24·0°, the concentration of the ammonium acetate varying from about normal upwards :—

	Molecules of salt per 1000 molecules of water—		
Density of solution	Ammonium acetate.	Ammonium sulphate	Lead acetate.
1·0197	20·0	0·54	0·52
1·0320	31·2	0·93	0·92
1·0457	44·5	1·49	1·46
1·0578	55·6	2·11	2·08
1·0694	68·5	2·77	2·74
1·1094	94·1	2·77	6·31
1·1281	133·3	2·80	8·10

The curve obtained does not agree with the formula developed by Noyes (*Amer. Chem. Soc.*, 1905, xxvii., 747), the solubility being greater than that given by the formula. The solid phase consisted of lead sulphate and was unaltered with concentrations of ammonium acetate up to rather more than 3N, but with more concentrated ammonium acetate, well-defined crystals of lead ammonium sulphate, $Pb(NH_4)_2(SO_4)_2$, were obtained.

The solubility of the lead sulphate increased considerably with ammonium acetate of greater concentrations than above, and the solid phases consisted of mixtures of lead sulphate and lead ammonium sulphate. The lead is probably present in solution as lead acetate, since the amount of sulphate in solution gradually became less than the equivalent of the lead present as the concentration of the ammonium acetate was increased beyond 3N.

161. "*Researches on Morphine.*" (Part III.) By FREDERIC HERBERT LEES.

In continuation of previous work (Schryver and Lees, *Trans.*, 1900, lxxvii., 1024 ; 1901, lxxix., 563 ; and Lees and Tutin, *Proc.*, 1906, xxii., 253), the author has shown that chloromorphide and bromomorphide yield chlorocodeide and bromocodeide respectively on methylation, the two latter bases previously obtained by other methods being simply the codeine analogues of the two former bases.

By the hydrolysis of chloromorphide, the author has isolated, besides β-*iso*morphine, an hitherto undescribed isomeride of morphine previously indicated by the hydrochloride ($[\alpha]_D$ −92·5°) obtained by Schryver and Lees. On methylation, this new base gives the so-called "ψ-codeine" (compare Merck, *Arch. Pharm.*, 1891, ccxxix., 161 ; Vongerichten, *Ber.*, 1903, xxxvi., 1591, and Knorr and Hörlein, *Ber.*, 1906, xxxix., 4409).

As the name ψ-morphine belongs to a well known oxidation product of morphine of which Merck's "ψ-codeine" is not the methyl ether or codeine analogue, the author has termed the new isomeride of morphine, *neo*iso*morphine* and its methyl ether, *neoisocodeine*

Neoisomorphine, $C_{17}H_{19}O_3N$, crystallises from alcohol in brilliant, prismatic needles containing one molecule of the solvent (m. p. 278°) ; its *hydrochloride*, $C_{17}H_{19}O_3N,HCl$, forms anhydrous crystals from alcohol ($[\alpha]_D$ −79·1° in water ;) its *methiodide*, $C_{17}H_{19}O_3N,MeI$, forms glistening crystals from alcohol (m. p. 297° ; $[\alpha_D$ −54·5° in water).

Neoisocodeine, $C_{18}H_{21}O_3N$, forms large colourless prisms from ethyl acetate (m. p. 181—182° ; $[\alpha']_D$ −96·6° in alcohol).

β-*iso*Morphine on methylation furnishes β-iso*codeine*, $C_{18}H_{21}O_3N$, which did not crystallise. The *methiodide*, $C_{18}H_{21}O_3N,MeI$, forms tabular crystals from water (m. p. 215—216° ; $[\alpha]_D$ −145·5° in water), and on boiling with sodium hydroxide readily yields a methine base.

It was also shown that the "*A-Base*" (m.p. 147—147·5° ; $[\alpha]_D$ −205·5° in chloroform) previously obtained by Lees and Tutin (*loc. cit.*) together with *iso*codeine (m. p. 171—172° ; $[\alpha]_D$ −155° in chloroform) by the hydrolysis of bromocodeide as a definite substance, not resolvable by re-crystallisation, is in reality a molecular combination of *iso*codeine and β-*iso*codeine.

PHYSICAL SOCIETY.

Ordinary Meeting, June 28th, 1907.

Prof. W. E. AYRTON, Past-President, in the Chair.

Mr. J. T. IRWIN gave a demonstration of the uses of his Hot-wire Oscillographs and Hot-wire Wattmeters.

After giving an explanation of the principle of the hot-wire oscillograph, and pointing out how to obtain exact compensation for the heat capacity of the wires by means of electric capacity or self-induction, Mr. Irwin showed the following experiments with the oscillograph :—

1. The P.D. from a rotary converter (*a*) with the ripples due to sparking damped out by resistance in the condenser-circuit, (*b*) with the ripples shown at their proper size with critical damping, (*c*) with the ripples very much exaggerated owing to want of damping.

2. The periodic discharge of a condenser through a self-induction (*a*) with a small resistance in circuit and therefore an oscillatory discharge, (*b*) with a large resistance in circuit and the oscillations damped out.

3. The P.D. across the stator of an induction-motor and the current in the rotor below, above, and at synchronous speed, (*a*) as a two-phase machine, (*b*) as a single-phase machine.

4. The current through and the P.D. across the armature of a single-phase commutating compensated motor run up to and above synchronous speed, (*a*) with the auxiliary brushes short-circuited showing the current and P.D. in phase with each other at synchronous speed, (*b*) with the auxiliary brushes open-circuited showing the P.D. and current differing by nearly 90° in phase.

5. A circle and a straight line produced by combining, by means of a beam of light, the vertical harmonic motion of a mirror with the simple harmonic motion of the oscillograph due to a sine wave of current, the circle being produced when the two movements were at 90° difference in phase, and the straight line when the two movements were in phase.

6. A hysteresis-loop for glass-hard steel wire, showing the rounding-off of the tips at a frequency of 40 per second.

Mr. Irwin also showed a new type of synchronous motor which he has invented and which can be run easily at synchronous or half-synchronous speed. This motor consists essentially of a series motor with laminated fields and with two points on the commutator 180 electrical degrees apart shorted.

A hot-wire instrument to measure mean watts was also shown.

Mr. W. Duddell expressed his interest in the fact that Mr. Irwin had succeeded in designing an oscillograph depending for its action on thermal effects. Referring to the hysteresis loops shown by the author, he said it was important to know the form of these loops in actual work. He was doubtful, however, whether the blunted points were due to hysteresis effects or whether they were due to instrumental defects.

Mr. A. Russell congratulated the author on his extremely novel and interesting instruments. Apart from the practical utility of the invention, which the experiments shown amply demonstrated, there were many points in connection with the working of the instrument which elucidated physical laws. For instance, in his paper to the Institution of Electrical Engineers, Mr. Irwin gave figures from which it could be deduced that Newton's law of cooling was very approximately true for the wire strips of his instrument slowly cooling in air. The practical working of his oscillograph proved that Newton's law of cooling was also very approximately true even when the periodic time of the temperature fluctuation of the strips was only a very small fraction of a second—a physical result of considerable importance.

Mr. J. S. Dow described a form of Photometer in which the cosine law was utilised. It was therefore unnecessary to move either the photometer or the sources of light. The adjustment of the illumination of the photometrical surfaces was carried out in the photometer itself by the rotation of a Ritchie wedge about the boundary-line between the photometrical surfaces as axis. The ratio of the candle-powers of the two sources of light compared could then be read off on a suitably calibrated scale attached to the photometer.

This type of instrument is very convenient. Attention was drawn, however, to the possibility of "angle errors" and the means of avoiding them.

This instrument could be used on the equality of brightness principle, or, by utilising an oscillating lens, as a flicker photometer. The results of using these two photometrical methods were, in this case, in very good agreement. Yet this might not have been the case if a different portion of the retina had been utilised, especially at low illuminations.

An experiment was then shown illustrating the behaviour of the "rods" and "cones" as regards flicker. At strong illuminations, when the cones are predominant, the perception of form and colour is most acute when the central portion of the retina is utilised; but at low illuminations, when the rods are in action, visual acuteness is best when the outer region of the retina is used.

In the same way the perception of flicker was demonstrated to be only most acute over the portion of the retina removed from the centre of the eye when a weak illumination is employed. A distinction must be drawn between "rod-flicker" and "cone-flicker."

Some experiments were then shown illustrating the detail-revealing powers of red and green light. A green or blue surface loses in luminosity as the image of it fades more and more towards the centre of the retina. But apart from the question of luminosity, the red end of the spectrum gives the best definition in the case of distant vision and the blue end in the case of very close vision. This arises from the want of achromatism of the eye.

Two exactly similar patches of red and blue light were thrown upon a screen on which a black and white chess-board pattern had been traced. The black and white squares were then seen to be more sharply defined when illuminated by the red light, in spite of the fact that the illumination due to the blue light was much the brighter of the two. The red end of the spectrum is therefore, in general, the most effectual portion for the illumination of clocks, shop-signs, and objects which must be viewed from a distance.

Mr. Patterson complimented the author upon his paper and experiments. With reference to the cosine instrument he asked if the cosine law was trustworthy at very acute incidence of the light. The unequal sensitiveness of different parts of the retina accounted for the fact that it was possible to obtain different balance-points by fixing attention on the different sides of a Ritchie wedge.

Mr. J. S. Dow, in reply, said he had only worked with photometers with wedges of 90°, but he was certain that the cosine law would not hold at acute incidence on account of the large amount of regular reflection.

A paper entitled "*Experiments on the Production of Sand Ripples on the Sea Shore*" was read by Mrs. Ayrton.

The sand-ripples which form so marked a feature of the sea-shore, although parallel to the line of the breakers, are not produced by their edges, but are formed entirely under water. It is difficult to imagine that the long, sweeping, to and fro motion of the sea that one watches from the beach, can produce row after row of quite small ripples, such as are seen in certain places on the beach. Yet it is this long, steady, see-saw motion of the water that produces the ripples, as was first observed in 1882 by Mr. Arthur Hunt.

To show this, a glass trough, six feet long, in which there was level sand, covered with a foot of water, was pushed to and fro on rollers by means of an electromotor. This motion set the water oscillating, and soon small ridges were seen in the sand, at nearly equal distances from one another, growing larger and larger as the oscillation continued.

Twenty years ago, Professor George Darwin discovered that certain vortices that he observed in water oscillating over ripples helped to build the ripples higher, but he left the problem of the *birth* of the ripples practically untouched. He thought that each ripple was started solely by friction, but this suggestion is apparently negatived by the regularity of the ripples, even in their earliest stages. By deduction from the shape of certain sand vortices, it appears that every ridge or furrow in otherwise smooth sand must produce two other ridges, one on either side of

the first, and that these two give rise to two other ripples, one on the right of the right-hand one, and the other on the left of the left-hand one, and so on, till the whole becomes ripple-marked. In other words, it wants but one *single* irregularity, in otherwise smooth sand, to cause the whole sand to become ripple-marked under oscillating water. Experiments were shown to demonstrate this fact.

Next, to show that the vortices generated by the original ripple actually swept out the succeeding ones, an artificial barrier was put across the trough to increase the size of the vortices, a handful of moist black pepper was thrown in, and the water oscillated. Immediately large vortices were seen whirling first on one side of the barrier, and then on the other, hollowing out furrows in the sand, while the great brushes of water that flowed over the vortices swept up new furrows. In fact, the actual process by which the water started and built up the ripples was shown.

Mrs. Ayrton illustrated how the sand ripples on the sea-shore could be exactly imitated, even when the water ran in one direction alone, if only the sand were sloped, as it is on the sea-shore, so that the water ran up it, and if, by means of a paddle, a series of waves were sent along the water in the direction in which it was running—if, in fact, the motion of the incoming tide were imitated. But if the long, surging motion of the sea produces the sand-ripples, why is not the whole of the sandy-shore seen ripple-marked? The answer is that it is all ripple-marked when the tide is high, but the waves at the edge of the retreating tide wipe out the ripples except where there is a pool, so that the water is left over the ripples until after the sea has retired. Further, while the water is oscillating over the sand-ripples, which it has formed, they never remain constant either in height, distance apart, or position. Their heights and distances apart are greater the more violent the oscillation, the longer it has been going on, and the greater the periodic time of the wave and the shallower the water. The greatest depth at which ripple-mark can be formed at the bottom of the sea depends on the violence of the motion of the water. At depths of 60 or 70 feet the sand is said to have been found ripple-marked. If the depth of a vessel is large compared with its cross section, a depth of water can be found beneath which no sand-ripples can be formed. In the case of a pickle-bottle, for example, this limiting depth of water over the sand is an inch or two.

During the whole of the demonstration the water in the 6-foot trough was kept oscillating, and the sand was seen to heap itself up in the form of a large ripple-marked heap at about the middle of the trough, having a contour very unlike that of the sea-shore ripples. On sprinkling a very little sand in the water in a small trough, and rocking it to and fro, the sand was seen to quickly assemble in a straight line across its middle. Watching these grains carefully, it may be noticed that the result arises from every swing carrying each grain on one side of the centre nearer to the middle than the next swing carried it away again. And not only each separate grain of sand, but each ripple as a whole, when ripples have been formed, tends to move towards the middle of the trough. In the 6-foot trough, and in a small trough, the water was kept oscillating so as to form a stationary wave twice the length of the trough, and the place where the heap of sand was formed was where the level of the water changed least and its horizontal velocity was the greatest. In a trough 3 feet long the water was oscillated by means of an electromotor, so that the length of the wave was only two-thirds the length of the trough, so that there were three places where the level changed least, and the horizontal velocity was a maximum, and at each of these three places the sand was seen to heap itself up.

Referring to the Goodwin Sands, which she had had an opportunity of observing, Mrs. Ayrton said she found it impossible to avoid recognising the resemblance between the hillocks and hollows of these sands and those made in her glass troughs, and it seemed, therefore, very possible that they were also produced by stationary waves. If so, then was it not possible, she asked, to imagine some means of altering the trend of the sea so as to keep it from forming the stationary waves which she believed heaped up the Goodwin Sands?

FARADAY SOCIETY.

Ordinary Meeting, June 25th, 1907.

Prof. S. U. PICKERING, F.R.S., in the Chair.

General Discussion on Hydrates in Solution.

AFTER some preliminary remarks by the CHAIRMAN, the Discussion was opened by Dr. T. MARTIN LOWRY, who read a paper on "*The Thermo-chemistry of Electrolytes in relation to the Hydrate Theory of Ionisation*," by Mr. W. R. BOUSFIELD, M.A., K.C., and himself.

1. The process of ionisation of a neutral salt in aqueous solution "*is usually attended with a development of heat*" (Nernst, "Theoretical Chemistry," 1904, 659), *e.g.*,

$$KCl \rightarrow \overset{+}{K} + \overset{-}{Cl} + 250 \text{ cals.}$$

(Arrhenius, *Zeit. Phys. Chem.*, 1889, iv., 106). It is pointed out that the decomposition of potassium chloride into molecular potassium and molecular chlorine involves an absorption of 105,600 cals., and that a further absorption must accompany the decomposition of the molecules into atoms. The electrification of the atoms is also probably an endothermic action, and the change represented by the above equation, so far from involving the liberation of 250 cals., must actually involve the absorption of more than 100,000 cals.

The process of ionisation must therefore involve some powerful exothermic action not shown in the ordinary scheme, and it is suggested that this is supplied by the combination of the charged atoms or "ionic nuclei" with the solvent to form hydrated ions.

2. A scheme is given whereby the work done in charging the ions, or in separating ions already charged, may be calulated on the assumption that the ions behave as charged conductors immersed in a fluid dielectric. The values deduced for the energy of electrification or of separation range from about 1000 to 8000 cals. per equivalent.

3. It is pointed out that, according to the theory of electrolytic dissociation, the heat of formation of a salt in dilute solution is the sum of the heats of formation of the ions. Values are deduced for the separate ionic heats of formation, and a table is given showing with what remarkable accuracy the additive law holds good; this additive relationship, which does not appear in the heats of formation of the solid salts, affords important evidence in favour of the view that the ions exist independently in dilute solutions.

4. The majority of the heats of formation of the ions are large positive quantities. The energy liberated during the process of ionising an element cannot be due to the disruption of the molecules of the element into atoms, nor to the electrification of these atoms. Both of the above processes appear to be endothermic, and it is again necessary, in order to explain the thermochemical data, to postulate that ionisation is accompanied by some exothermic action not indicated in the symbols—

$$\frac{K_x}{x} \rightarrow \overset{+}{K} \quad \text{or} \quad \frac{Cl_2}{2} \rightarrow \overset{-}{Cl}.$$

This exothermic action is supplied by the combination of the ionic nucleus with the solvent.

Dr. JAMES C. PHILIP, M.A., Ph.D., D.Sc., read a paper entitled "*Influence of Non-electrolytes and Electrolytes on the Solubility of Gases in Water. The Question of Hydrates in Solution.*"

The author supported the view according to which the diminished power of a solution to dissolve hydrogen and oxygen as compared with pure water is due mainly to the hydration of the solute and the consequent diminution of the "free" solvent. In determining the extent to which

any given solute is hydrated, it is first supposed that the standard absorbing volume is, not 1 litre of the solution, but that volume of the solution which contains 1000 grms. of the pure solvent. In this way values of the average molecular hydration for a number of common salts are obtained. It is found that the average molecular hydration increases with the dilution of the salt solution, and decreases for a given salt solution as the temperature rises.

Dr. George Senter read a paper on "*Hydrates in Solution: Discussion of Methods Suggested for Determining Degree of Hydration.*"

It is pointed out that recent attempts to account for the properties of aqueous solution on the basis of association alone have not only proved inadequate to afford a quantitative representation of the facts, but in some respects do not appear to be even in qualitative agreement with experiment.

In forming an opinion as to the relative trustworthiness of different methods which have been suggested for determining the degree of hydration regard must be had to the following considerations: (1) Other things being equal, statical methods are more reliable than dynamical ones; (2) the law of mass action requires that for salts the degree of hydration must increase with dilution up to a point beyond which it remains practically constant on further dilution; (3) if, as is usually the case, hydration is associated with evolution of heat, the complexity of the hydrates must decrease with rise of temperature.

All the different methods indicate that the degree of hydration varies with the atomic weight; for example, in the case of the chlorides of the alkalis, the hydration decreases with increasing atomic weight of the alkali metals. From a quantitative point of view our knowledge of hydration is much less satisfactory, and the results so far obtained must be regarded as of a preliminary character.

A paper communicated by Dr. Alex. Findlay on "*The Stability of Hydrates as Indicated by Equilibrium Curves*" was read in abstract by the Secretary.

From a study of the freezing-point curves of concentrated aqueous solutions conclusions have been drawn, more especially by Biltz and by H. C. Jones, with regard to the existence of hydrates in solution. While the qualitative correctness of the conclusions may be accepted, grave doubts arise as to the correctness of the quantitative formulæ assigned by Jones to the hydrates of different substances. These doubts are due not only to the fact that the conclusions as to hydration were reached (in so far as the freezing-point measurements are concerned) by means of an unjustifiable extension of the van 't Hoff-Raoult law, but also to the fact that certain factors, *e.g.*, heat of dilution, were not taken into account.

While the study of the equilibrium curve of solutions in contact with ice as solid phase (the freezing-point curve) may, on the basis of certain assumptions, give an indication of the "degree of hydration" of the solute, it cannot enable us to decide as to the particular hydrates present, nor the extent to which these hydrates are dissociated chemically.

On the other hand, some insight into the question of the stability of hydrates can be obtained from the study of the equilibrium curves of solutions in contact with the hydrates as solid phase, *i.e.*, what are frequently called solubility curves.

When a compound of two components is capable of existing in contact with solution of the same composition as itself, *i.e.*, when it possesses a definite melting-point, the equilibrium curve of the two-component system will exhibit an intermediate curve, which gives the conditions under which the solid compound can exist in contact with the liquid solution, or homogeneous mixture of the two components. When the compound undergoes chemical dissociation at the temperature of the melting-point, it is found that the equilibrium curve has a rounded summit, and the greater the degree of dissociation the flatter is the summit of the curve. Conversely, the sharper the summit of the curve the less the degree of dissociation. From the appearance of the curve alone, then, some idea of the stability of the compound can be obtained.

If, now, we regard the presence of the products of dissociation as causing a lowering of the freezing-point of the pure compound, and if we regard the lowering produced to be in accordance with the van 't Hoff-Raoult law, then, from a knowledge of the molecular depression of the compound, it is possible to calculate the course of the freezing-point curve of the compound for different degrees of dissociation. The experimentally determined equilibrium curve is compared with the curve so obtained, and thus an approximate knowledge obtained of the degree of dissociation of the compound.

It must be pointed out that this method of determining the degree of dissociation is only an approximate one, for it depends on various assumptions which cannot be regarded as being more than approximately fulfilled. The chief of these assumptions are:—(1) the validity of the van 't Hoff-Raoult law, (2) the validity of the law of mass action in concentrated solution, (3) the degree of dissociation is independent of the temperature.

So far calculations have been carried out only in the case of organic binary compounds; but the method can also be applied to the case of salt hydrates, although in this case the above assumptions are less likely to be fulfilled.

Prof. W. A. Tilden, F.R.S., referred to the fact that in crystals it appeared to be the metal only which detained the water of crystallisation. In many cases, such as that of ammonia dissolved in water, where ammonia as such was also present, the hydrate theory could not be adopted as it stood. There was, in fact, no single theory at present able to explain all the phenomena observed.

Mr. Caldwell criticised the various methods used for measuring hydration. In the experiments of Jones, for example, whose method was open to objection, many of the results did not follow what would be expected from the law of mass action. Philip assumed that the dissolution of a gas was mechanical and that of a salt chemical. If that were true a gas of small molecular weight, such as helium, should be readily soluble.

Mr. W. A. Davis said that there were many cases of solution, *e.g.*, in dyeing, which were covered by neither the ionic nor the hydration theory, but in which the process was purely mechanical.

Mr. Fenton said that it was not always very clear what was meant by a hydrate. The methods hitherto employed for studying hydrates were chiefly physical, and the results obtained were capable of many interpretations. The problem should be studied in such a way that specific chemical properties were obtained.

In reply to Dr. H. Borns, Dr. Lowry said he imagined ionisation to be the result of the separate hydration of the ionic constituents of the molecule.

The Chairman thought that the agreement between the heat of formation of a salt in dilute solution and the sum of the separate heats of formation of the ions shown to exist by Mr. Bousfield and Dr. Lowry proved nothing, as the proof involved reasoning in a circle. In reply, the authors explained that the agreement proved these properties of the ions to be additive, and so gave further support to the dissociation hypothesis.

Battersea Polytechnic.—The Governing Body of the Battersea Polytechnic have appointed Mr. S. G. Rawson, D.Sc. (Lond.), F.I.C., Principal of the Polytechnic in succession to Mr. Sidney H. Wells, who has been Principal since the foundation of the institute in 1893, and is resigning to take up the position of Director-General of the Department of Agriculture and Technical Education for Egypt. Dr. Rawson is at present Director of Education for Worcestershire, and was formerly Principal of the Technical College, Huddersfield, and Lecturer at Liverpool University.

OBITUARY.

SIR WILLIAM HENRY PERKIN, F.R.S.

The news of the death of Sir William Perkin, of pneumonia and appendicitis, after an illness of four days' duration, will be received with the deepest regret by the whole scientific world. His researches have made his name universally known and revered, while in those who enjoyed the advantage of personal acquaintance with him his singularly charming disposition evoked no less admiration.

Sir William Perkin, who received the honour of knighthood last year, was the youngest son of Mr. G. F. Perkin, and was born in London in 1838. He was educated at the City of London School, and passed thence to the Royal College of Chemistry, where his conspicuous ability soon brought him prominently before the Principal, Professor Hofmann, who soon after his entrance appointed him to the post of private assistant, and in every respect did his utmost to stimulate and direct the ambitions of the boy. Perkin had from the beginning been deeply interested in chemistry, and the influence of Professor Hofmann was soon sufficient to increase his liking to a passion, in the pursuit of which his ardour knew no flagging, and from the very early days of his career as a student of the College he devoted much of his spare time and energy to the study of various problems which the course of lectures he was attending suggested to his active mind. During one vacation he was studying the synthesis of quinine, when he found that the oxidation of aniline with potassium bichromate and sulphuric acid leads to the formation of a dye, mauvéine, afterwards shown to be phenyl-safranine. When a favourable opinion of the value of this new colouring matter had been expressed by dye experts, in spite of the many difficulties with which he was confronted, Perkin, with the aid of his father and brothers, established a factory at Greenford Green, near Harrow, in which the new substance could be prepared on a large scale, and within a year of its discovery he succeeded in placing it upon the market—a remarkable achievement indeed for a youth of eighteen. The discovery of mauve gave a great impetus to the investigation of coal-tar and its derivatives, and laid the foundation of the most important of scientific industries. Perkin's work was soon followed by researches, undertaken by the chemists of all nations, and leading to the discovery of various derivatives of triphenyl-methane.

Meanwhile he was pursuing the investigation of different classes of organic substances, and was showing particular skill in devising and perfecting new methods of synthesis. Thus he found that by the action of aromatic aldehydes upon the salts of fatty acids it is possible to synthesise unsaturated acids, and this reaction, which is now known by his name, has led to important developments in technical chemistry. When he applied it to salicylic acid and sodium acetate he obtained the sodium salt of coumaric acid, and from the latter by elimination of water the anhydride coumarin is prepared. This substance was the first natural perfume prepared synthetically, and Perkin was thus instrumental in setting on foot the artificial perfume industry. The study of these condensation reactions is still yielding rich fruit, both from a purely scientific and a commercial point of view. Another dye manufactured for the first time on a commercially remunerative scale in the Greenford factory was madder red or alizarin, the laboratory preparation of which from anthracene had been discovered by Graebe and Liebermann, and turned to practical account by Perkin. Moreover, his work upon the rotation of the plane of polarisation by a magnet, and upon the relations between magnetic polarisation and chemical constitution, has brought to light some important facts.

Enough has been said of some of the more striking results of Perkin's work to indicate how he possessed a remarkable power of recognising the commercial possibilities of scientific work, while at the same time he never ceased in his allegiance to purely scientific research, and of late years had devoted himself exclusively to it. He discovered and threw valuable light upon the constitution of many substances of great importance in organic chemistry, and thus did much to further its development from a purely theoretical point of view. It is, perhaps, unnecessary to recall how honours of all descriptions were showered upon him, reaching their culminating point last July in the Jubilee celebration of the foundation of the coal-tar industry, when he received gratifying evidences of the esteem and admiration felt for him by the whole scientific world. A presentation of his portrait, which now becomes the property of the nation, of addresses from many scientific institutions of all nations, and the foundation of a fund for the promotion of chemical research, to be known by his name, were among the practical manifestations of the regard in which he was held, while various marks of recognition of his valuable work were received by him from foreign chemical societies, and the universities of all nations vied with one another in conferring honorary degrees upon him.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 24, June 17, 1907.

Preparation of Anhydrous Lithium Oxide.—M. de Forcrand.—If the heat of solution of lithium oxide is taken as 26 cals. (Berkétoff) and 8·96 cals. for the solution of $Li_2O.H_2O$ or 2LiOH, by difference $Li_2O(sol.) + H_2O(liq.) = 2LiOH(sol.) + 17·04$ cals. From this it would appear that the dehydration of lithium hydroxide by heat would give the anydrous oxide, Li_2O. Thus, adding 9·66 cals., the heat of formation of H_2O gas, we get 26·70 cals. for the reaction $Li_2O + H_2O(gas) = Li_2O.H_2O(sol.)$. Now, $\frac{26,700}{30} = 890°$ (abs.) = 617° C. Thus, LiOH should boil at 617°, and if the water vapour generated were removed by an inert gas the complete dehydration should be effected below 600°. These theoretical considerations have been confirmed by the experimental facts. If pure commercial lithium hydroxide or the crystalline secondary hydrate, $LiOH.H_2O$, is heated in a current of hydrogen at a temperature of 660°, the dehydration commences rapidly, then slackens, and is complete after seven or eight hours. At 780° the same result is obtained in one hour. There is no loss by volatilisation, and the platinum boat in which the operation is carried out is unaffected, though at 800° or 820° a loss of weight can be detected. The substance thus obtained is absolutely white, not crystalline but porous; its analysis gives the formula Li_2O exactly.

Absolute Atomic Weight of Manganese.—Gustavus D. Hinrichs.—Baxter and Hines find for the atomic weight of manganese 54·951 to 54·959, *i.e.*, approximately 0·05 below 55. If Ag = 108, Br = 80, Mn = 55, the value $\frac{2Ag}{MnBr_2} = 1·00465$ change = −47, variation = 2·13. It is then found that Baxter and Hines' experiments give a mean variation of −1 in the fifth decimal place of the ratio $Ag : MnBr_2$. Thus, the absolute atomic weight of manganese is 55 according to Baxter and Hines' fifteen experiments, when they are examined by the author's method. It is interesting to notice that the very small variations differ in magnitude and even in sign according to the degree of purity and origin of the material used, which goes to prove the accidental nature of these deviations. The second series of experiments in which the ratio

$\frac{2AgBr}{AgBr_2}$ was determined gave a change of −82 and a variation of +1·22 (for 0·1 in manganese), and thus the agreement was not so good as in the first series, probably because the reaction is too complex.

Arsenic and Methyl Arsenic Acids.—E. Baud and A. Astruc.—The authors have determined the heats of solution of pure arsenic acid and its anhydrous sodium salts, as well as the heat of neutralisation of the dissolved acid by one, two, or three molecules of soda in solution. For arsenic acid the numbers obtained are:—

$AsO_4H_3(sol.) + Na(sol.) = H(gas) + AsO_4NaH_2(sol.)$ + 57·15 cals.

$AsO_4NaH_2(sol.) + Na(sol.) = H(gas) + AsO_4Na_2H(sol.)$ + 45·87 cals.

$AsO_4Na_2H(sol.) + Na(sol.) = H(gas) + AsO_4Na_3(sol.)$ + 40·76 cals.

Arsenic acid is therefore a little less acid than phosphoric acid, but the difference is relatively small. For cacodylic acid

$$O=As(CH_3)_2(sol.) + Na(sol.) = H(gas) + OAs(CH_3)_2(ONa)(sol.)$$ + 41·72 cals.

Thus, the following results have been obtained:—(1) Mean acidity of arsenic acid, 47·92 cals.; (2) mean acidity of monomethyl arsenic acid, 44·705 cals.; (3) mean acidity of cacodylic acid, 41·72 cals. Hence, the fixation of a CH_3-group to the atom of arsenic diminishes the acidity of arsenic acid by 3·22 cals., and the fixation of a second group again lowers it by 2·98 cals. These numbers agree perfectly with the rule suggested by De Forcrand for the acidity of alcohols.

Action of Fluorine on Selenium in presence of Glass.—Paul Lebeau.—The author's chief reason for believing that Prideaux's hexafluoride of selenium is really an oxyfluoride is the fact that when the gas from several preparations is fractionated in such a way as to collect in different flasks the more or less volatile products, a decided difference of density is found in the contents of the flasks—the first portions have a density of about 6·59 (the theoretical density), while in the last portions it falls as low as 6·28. From a chemical point of view the analysis of the gas presents special difficulties, but the author hopes to communicate shortly the results of his experiments.

Solubility of Alumina in Aluminium Sulphide and of Magnesia in Magnesium Sulphide.—Marcel Houdard.—If aluminium sulphide is fused with alumina in an electric furnace and the melt is treated with dilute hydrochloric acid, an insoluble crystalline residue of alumina remains behind. If the mass is allowed to cool sufficiently slowly, rhombohedric crystals are obtained. Attempts to colour these crystals have not as yet been successful. Crystals of magnesia can be prepared similarly. Concentrated hydrochloric and nitric acids slowly dissolve crystalline magnesia when warmed; sulphuric acid acts upon it in the cold. The crystals are cubic, and have no action on polarised light.

Glycol of Anethol. Transformation into Anisylacetone.—MM. Tiffeneau and Daufresne.—If an acetic solution of anethol dibromide is boiled with zinc acetate a molecular transposition occurs, and *p*-methoxyhydratropic aldehyde is formed:—

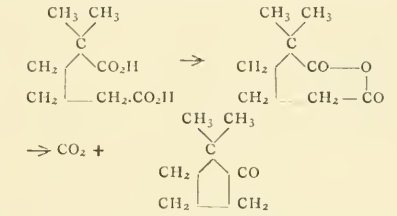
$$OCH_3—C_6H_4—CH_2(CO_2—CH_3)—CHBr—CH_3 \xrightarrow{-HBr} OCH_3—C_6H_4—CH_2(CO_2—CH_3)—C(CH_3)=CH_2$$

$$\rightarrow OCH_3—C_6H_4—C(CH_3)=CH—CO_2—CH_3) \xrightarrow{+CH_3CO_2H} OCH_3—C_6H_4—CH<CH(CO_2CH_3)_2.$$

The saponification of this diacetic ether gives directly the glycol of anethol, fusing at 116°. When distilled *in vacuo* it loses water, yielding a crystalline compound which seems to be the corresponding diethylene oxide. The authors submitted this glycol to the action of sulphuric acid and investigated the product obtained. Silver oxide transforms it into anisic acid; with iodine and caustic potash it gives iodoform and methoxyphenylacetic acid. Its semicarbazone and oxime fuse at 175° and 74° respectively. Hence, the glycol of anethol is transformed into anisylacetone according to the equation:—

$$OCH_3—C_6H_4—CHOH—CHOH—CH_3 = H_2O + OCH_3—C_6H_4—CH_2—CO—CH_3.$$

New Method of Converting Substituted Adipic and Pimelic Acids into Cyclic Compounds.—H. G. Blanc.—The method of passing from dibasic acids to the corresponding cyclic ketones by calcination of the calcium salts is inconvenient from many points of view. The author finds that it is both simpler and quicker to heat the acid (*e.g.*, substituted adipic acid) for some hours with acetic anhydride, thus getting the anhydride. Then the excess of acetic anhydride is driven off *in vacuo*, and the anhydride of the dibasic acid is decomposed by slow distillation at ordinary pressure:—



The yield with adipic and pimelic acids is not very satisfactory (about 50 per cent of the theory), possibly because the ketones readily condense. The author has thus prepared some new ketones, which form the starting-point for the synthesis of terpene derivatives.

Dimagnesium Compound of Dibromopentane-1.5.—V. Grignard and G. Vignon.—Dibromopentane in presence of anhydrous ether reacts easily with powdered magnesium, giving a magnesium compound, hardly soluble in ether, which separates as a slightly coloured mobile liquid. Carbon dioxide is absorbed in the cold with a slight evolution of heat, and a crystalline mass forms in the lower liquid layer. From this an acid and a neutral portion can be separated. The latter distils at 50—52° under 12 mm. pressure, and cyclohexanone is the principal product of the reaction. When the acid portion precipitated from its sodium salt is fractionated, from the product may be separated dimethylene dicarboxylic acid. The equations are:—

$$CH_2<CH_2—CH_2MgBr / CH_2—CH_2MgBr + CO_2 = CH_2<CH_2—CH_2>C<OMgBr / OMgBr$$

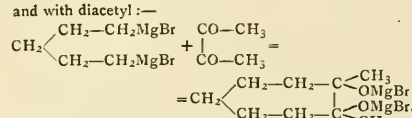
$$\rightarrow C_6H_{10}O + MgBr_2 + MgO$$

$$CH_2<CH_2—CH_2MgBr / CH_2—CH_2MgBr + 2CO_2 = CH_2<CH_2—CH_2—CO_2MgBr / CH_2—CH_2—CO_2MgBr.$$

With ethyl acetate the dimagnesium compound undergoes the following reaction:—

$$CH_2<CH_2—CH_2MgBr / CH_2—CH_2MgBr + CH_3CO_2C_2H_5 = CH_2<CH_2—CH_2>C<OMgBr / CH_3 + C_2H_5OMgBr.$$

and with diacetyl :—



Cathode Phosphorescence of Complex Systems.—G. Urbain and Clair Seal.—The authors have studied the phenomena of cathodic phosphorescence in mixtures with the following results :—*Coloured Mixtures.*—The presence of coloured oxides (of terbium or praseodymium) diminishes the phosphorescence due to other substances, the influence of terbium oxide being much greater than that of praseodymium. Samarium oxide and dysprosium oxide, which are nearly white, mask the phosphorescence of the black oxide of praseodymium, but to a lower degree than black terbium oxide. The maximum of phosphorescence due to each substance in a ternary system corresponds to the percentage of substance necessary to produce the maximum in binary systems with the same diluent. The maximum is less bright in a ternary than in a binary system. Spectral variations due to dilution are the same in binary as in ternary systems. *Colourless Mixtures.*—The oxides of praseodymium and terbium, which are black, are necessarily very absorbent, but their salts behave practically like colourless substances in ternary phosphorescent mixtures. The phenomena due to dilution and to the reciprocal independence of the maxima are the same in these mixtures, but the salts of praseodymium do not mask the phosphorescence of samarium, terbium, and dysprosium. On the contrary, the salts of these last three elements mask not only praseodymium but also the other rare earths.

MISCELLANEOUS.

Queen's College, Galway.—Mr. Percy Corlett Austin, M.A., of Queen's College, Galway, has just been awarded a Science Research Scholarship in Organic Chemistry by His Majesty's Commissioners for the Exhibition of 1851 ; and Mr. William Goodwin, B.Sc., Ph.D., a former 1851 Exhibition Research Scholar of Queen's College, Galway, has been appointed Lecturer in Chemistry at the South-Eastern Agricultural College, Wye, Kent.

Society of Arts.—The Council of the Society of Arts have awarded medals to the following readers of Papers at the meetings of the Session just concluded :—

To Mr. John William Gordon, for his paper on "Patent Law Reform."

To Colonel Sir Charles M. Watson, K.C.M.G., CB., for his paper on "Some Objections to the Compulsory Introduction of the Metric System."

To Mr. Albert E. Humphries, for his paper on "Modern Developments of Flour-milling."

To M. Philippe Bunau-Varilla, for his paper on "The Panama Canal—the 'Lock Canal' type and the 'Straits of Panama' type."

To Mr. Arthur E. Morton, for his paper on "Modern Type-writers and Accessories."

To Mr. Noel Heaton, B.Sc., for his paper on "Mediæval Stained Glass, its Production and Decay."

To Mr. Herbert Wright, for his paper on "Rubber Cultivation in the British Empire."

Mr. Alfred Edward Carey, M.Inst.C.E., for his paper on "The Protection of Sea Shores from Erosion."

To Mr. A. Yusuf-Ali, M.A., LL.M., I.C.S., for his paper on "The Indian Mohammedans — their Past, Present, and Future."

To Captain E. Barnes, for his paper on "The Bhils of Western India."

To Sir Frederic S. P. Lely, K.C.I.E., C.S.I., for his paper on "The Practical Side of Famine in India."

To Mr. Laurence Robertson, I.C.S., for his paper on "Irrigation Colonies in India."

To Mr. George Wilson, C.B., for his paper on "The Progress of the Uganda Protectorate."

To Hon. John Winthrop Hackett, LL.D., for his paper on "Social and Economic Conditions in Australia."

To Mr. Thomas Okey, for his paper on "Basket Making."

To Mr. William Dale, F.S.A., for his paper on "Artistic Treatment of the Exterior of the Pianoforte."

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DIAMONDS.

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2487.

VULCANISATION TESTS WITH PLANTATION RUBBERS.

By CLAYTON BEADLE and HENRY P. STEVENS.

When a raw material which for many years has formed the staple of a large industry is by force of circumstances produced in new districts and by new methods, the manufacturer naturally asks himself whether his new sources of supply are suitable to his methods of manufacture. He may, of course, have no difficulty in determining which of the products (*i.e.*, from old or new sources) is best suited to his *existing* methods, which methods are the result of a long experience with his original sources of supply; but it becomes ultimately a question as to which product will suit him best in the long run if both are worked under the most favourable conditions.

This is the state of affairs in which the rubber industry in the course of time will find itself, or more particularly that branch of the industry which deals with the production of high-class rubber articles of which para-rubber is an important ingredient. Up to within the last three or four years the world drew its supply of raw rubber from trees growing wild in various tropical areas. Some ten years ago a beginning was made with planting—particularly in the Malay Peninsula, and later in Ceylon—chiefly with *Hevea Brazilicnsis*, or the para-rubber tree, but as no commercial yield of rubber is obtained until the tree reaches its fifth or sixth year the effect of this planting is only just beginning to be felt, and the imported plantation rubber at the present time only forms about 1 per cent of the total production. From the large areas now in process of being opened up, this production must increase considerably in the course of the next ten or fifteen years, until eventually the plantation rubber forms a considerable proportion of the supplies to rubber manufacturers.

The properties of rubber are not only dependent upon such things as soil, locality, climate, &c., but are largely affected by the methods used in curing and preparing it for the market, and as the methods of coagulation and preparation differ radically from those used in the case of wild rubbers this consideration particularly applies to plantation rubber. Without going into any details it may be stated that in the former case the methods are primitive and inadequate, except in the case of the smoked rubbers, while the planters by commonsense precautions, and in some cases by the use of simple coagulating, washing, and drying plant, have sent to this country consignments which are unequalled from the point of view of purity and general excellence. It has, however, been asserted, without apparent reason, that, in spite of these desirable qualities, the plantation rubber is wanting in the "nerve" especially attributed to hard cure para.

The object of the present paper is the discussion of a number of preliminary tests made with the plantation rubber with a view to testing its qualities and comparing it with a typical high-class rubber, such as hard cure Amazonian para. The methods employed in valuation of rubbers as carried out by brokers and merchants would be useless for this purpose. The broker looks for adulterants, and tests the physical qualities by the general appearance, smell, and feel of the rubber. Such tests cannot, except in the roughest manner, be of any value in forming an estimate of the qualities of plantation or any other rubber from a manufacturer's standpoint. A carefully conducted chemical analysis will, however, be of some help.

It is obvious, to begin with, that the value of a crude rubber to the manufacturer will to a large extent depend upon the proportion of actual rubber substance or caoutchouc it contains (see Heil and Esch, "Handbuch der Gumm Warenfabrikation," p. 40). A crude rubber, such as hard-cure para, will contain certain substances normally present in the latex from which it was obtained; of these the most important are resin and protein or nitrogenous bodies. It may also contain extraneous substances, such as sand and dirt of all kinds, and finally it will always contain more or less water. It is usual to determine these constituents and by difference to calculate the amount of caoutchouc, there being no agreed satisfactory method of directly estimating the latter. It has been suggested that a further examination should be made of the resin and protein bodies with a view to characterising them more exactly; but, quite apart from the large amount of research work which will be necessary before this can be done, it is difficult to see what advantage will be gained except for the purpose of distinguishing the source of the rubber; in any case it is doubtful if the results would justify the additional work entailed in the analysis.

Table I. gives the analysis of a typical hard cure para and that of a plantation "block"; the latter represents the mean of numerous analyses we have made from time to time on good qualities of this product.

Table I.

	Hard-cure para.	Plantation "block," as imported.
Moisture	12·7	0·4
Resins..	3·1	4·0
Protein	2·9	2·8
Ash	0·3	0·1
Caoutchouc (by difference)	81·0	92·7

It will be seen that the figures are distinctly in favour of the plantation product; the moisture is particularly low in the latter owing to its having undergone a systematic drying process. This has the great advantage that the rubber is much less likely to undergo putrefactive change during transport through hot climates—as everyone knows—moulds and bacteria must have moisture for their growth and development. The samples we have examined of properly prepared wild rubber all contained large quantities of water, such as from 10 or 12 per cent. Of course, plantation rubber which is merely air-dried, as in the form of biscuits, may contain more than one-half per cent moisture, but the amount will not be excessive.

So far, then, as the analyses go, the figures are in favour of the plantation, and this has found due recognition on the market, where the best dry block, crepe, and other forms have fetched a higher price than hard cure para, practically in proportion to the percentage of real rubber that these products contain. It may, however, be questioned whether a greater difference in price is not justifiable and will be obtained in favour of plantation rubber when the advantages of a pure and regular product are better recognised and manufacturers have acquired greater experience and confidence in handling it.

As the best block, crepe, and sheet are washed in a two-roll washing machine immediately after coagulating, and then dried either in the air or in vacuum drying ovens, and this treatment on the spot is becoming very general, it seems reasonable to suppose that the manufacturer in this country should be able to take this washed and dried product and use it straight away in his mixing machines without any preliminary treatment. On the other hand, all ordinary grades of wild rubber when received by the manufacturer are too impure and contain too much moisture for use right away; they have therefore first to be subjected to a washing process in which the rubber is torn to shreds, in the course of which its "nerve" is affected, and then subsequently to be submitted to a tedious drying process, and if possible storage, in order that the rubber may regain

some of the physical properties it has lost on treatment. Not only is it natural to suppose that all this can be avoided by the use of rubber washed and dried on the plantation, but the loss incurred in the washing process is also avoided. This loss in the case of the best wild rubbers, such as hard-cure para, amounts to from 13 to 17 per cent.

In order to test the value of plantation grown and plantation prepared rubbers, something more is required than chemical analysis. As for practical purposes it may be said that all rubber is vulcanised in the course of manufacture, and as the properties of vulcanised rubber are very different from the raw article, it appeared to us that the only satisfactory means of determining the value of plantation rubber was to vulcanise it, and carry out physical and chemical tests on the vulcanised product. Moreover, in order to eliminate as far as possible the effect of carrying out such vulcanisation on a laboratory instead of on a manufacturing scale, we made a number of parallel experiments with a sample of typical hard-cure para, which was treated throughout in an exactly similar manner to the plantation rubber. Not only can we test the qualities of plantation rubber in this manner, but we are able to put to the test the possibility of mixing and vulcanising washed and dried plantation rubber without any preliminary treatment.

The hard-cure para was, of course, washed and dried previous to vulcanising, as no results could be got with a product containing moisture. To accomplish this, the wild rubber was cut up, soaked in luke-warm water for some time, and then disintegrated and torn up to shreds in a stream of water, after which it was dried first in air, and subsequently in a desiccator, where it was preserved during the course of the experiments. By these means we imitated as far as possible the methods of purification employed by manufacturers.

The masticating and mixing operations were carried out in a specially equipped machine, which was found well suited for treating small quantities for experimental purposes, and no difficulty was experienced in obtaining a thoroughly even and homogeneous mass. The machine was arranged so that it could be steam heated and kept under proper control. As some of the experimental results obtained by Continental workers are open to criticism owing to the small amount of material used, in our experiments not less than 50 grms. of material were operated upon at a time to minimise any error due to loss of sulphur or loading to be incorporated with the rubber. Some Continental authorities have taken 5 grms. of rubber per mixing. Under such circumstances a loss of finely powdered sulphur or mineral is sure to take place; when the quantities operated on are very small the percentage loss may be considerable. Thus, 5 grms. of rubber would require, say, only 0·3 grm. of sulphur, and a loss of 0·05 grm. would reduce the percentage of sulphur incorporated with the rubber from 6 to 5 per cent; such a difference would entirely vitiate the results. As the amount of mastication very considerably influences the nature of the product in comparative tests, the mastication and mixing was continued for the same length of time. It has been shown that prolonged mastication will increase the acetone soluble products (so-called resins) by as much as 1 per cent. This matter, however, requires further investigation. In most cases when working with plantation rubbers without the addition of mineral matter, the treatment during mastication and mixing seems to have more effect on the product than the time of vulcanisation, provided that it is kept within the usual safe limits; that is to say, it would appear that changing from two to three and four hours' vulcanisation had a smaller influence on the tensile strength of the product than a difference in treatment in mastication and mixing. These points require more experimental work, which is in progress, but will not be discussed in this paper. We shall merely deal here with the general results.

The mixture, after kneading and while still hot, was forced into an iron cylinder. The bottom of the cylinder was closed with a screw-cap, and by means of a steel plunger the mixing was compressed into a solid cylindrical block of such a size that slices could be cut off to fit into the vulcanising moulds. The moulds are of similar construction to those used on a large scale.

On a manufacturing scale it is usual to give the digester a gradual "rise"; that is to say, the temperature is never suddenly raised, but is taken up to one corresponding to a certain pressure, say, for one hour before raising it further. We have tried both slow and rapid methods with mixings containing little or no mineral, and have not found the gradual raising of the temperature to influence the strength of the product to any very marked degree. On the other hand, care, of course, must be taken to keep the temperature within certain defined limits.

For tensile strengths much difficulty was experienced in testing small strips, owing to the tendency of the rubber to tear and rupture in the jaw, even when the ends were cut considerably wider than the middle portion. Eventually the difficulty was got over by punching small rings, which were stretched between smooth round iron hooks. The testing machine was constructed on the well-known principle used in testing cement and other materials, where a regular stream of water or shot is allowed to run into a vessel and the supply cut off automatically the moment of rupture. All figures given are the mean of at least ten tests.

Having briefly described the experimental methods employed we now proceed to give a short *résumé* of the results so far obtained.

The products prepared from plantation rubber were of a beautifully clear transparent yellow to brown shade when viewed through sheets 1 mm. thick. Those prepared from hard-cure para were much darker and less transparent. When vulcanised for a short time the surface sulphured up in the ordinary manner. In the course of our work so far we have carried out over 150 vulcanisations. We have subjected twenty separately vulcanised samples of plantation rubber containing only rubber and sulphur without mineral or other additions to tests for tensile strength and elongation at the moment of rupture, details of which are given in Table II.

TABLE II.—*Tests on Vulcanised Plantation Rubbers.*

Vulcanisation reference number.		Sulphur, per cent.	Tensile strength, in grms.		Elongation at rupture when original = 1·0.		Elongation under a strain 1500 grms. when original = 1·0.	
48			3129		—		—	
49	L	6	3574	3278	13·4	13·0	8·7	8·3
62			3133		12·7		8·0	
74			2882		13·9		—	
77	Q	6	3015	2933	13·3	13·4	9·4	9·7
79			2910		13·2		9·4	
80			2927		13·1		10·2	
83			3164		12·4		8·2	
85	R	6	3263	3264	12·4	12·5	8·0	8·9
87			3366		12·7		9·5	
99			3320		13·3		8·5	
104	T	6	3168	3349	12·5	12·9	8·2	8·2
92			3499		13·1		7·9	
94			3410		12·9		8·2	
143	D2	6	3260	3120	13·4	13·4	10·2	10·4
144			2981		13·4		10·6	
101			3138		13·7		10·4	
45	K	5	3428	3245	14·3	14·0	9·5	10·1
139			3169		13·9		10·4	
110	X	8	3324	3324	12·0	12·0	7·7	7·7
Mean of all tests			3203		13·1		9·0	
Mean of L, Q, R, T, and D2			3187		13·0		8·9	

Taking first the tensile strength in grms. required to rupture the rings, the average of the whole series works out to 3203, and the elongation at the moment of rupture 13·1 per cent. Of these samples, sixteen were vulcanised with 6 per cent of sulphur, and gave an average strength of 3187 grms. and an elongation of 13·0 per cent. Three vulcanised products (K) containing 5 per cent of sulphur were tested, and gave an average tensile strength of 3245 grms. and elongation 14 per cent, while the sample vulcanised with 8 per cent gave a tensile strength of 3324 grms. and elongation of 12 per cent. Although the figures for tensile strength of K and X are somewhat higher than the average of the remainder (3187), we do not attach great importance to this, as this latter average is pulled down by the uniformly low results obtained with mixing Q, and due to some irregularity in the mixing process. On the other hand, it is noteworthy that K (with 5 per cent sulphur) gives a greater elongation (14·0 per cent) than the average (13·0 per cent), while X (with 0·8 per cent of sulphur) gives a smaller elongation (12·0 per cent).

We come now to vulcanising tests with fine hard cure para. We are indebted to Mr. Devitt, jun., of the firm of Lewis and Peat, for supplying us with a quantity of a good average sample of the above, and valued early in March last at 5s. 1d. per pound. (The analysis of this sample is given above). After washing and drying, the mixing and vulcanisation of the samples was carried out in exactly the same manner as with the plantation rubber. The results of the tests are given in Table III.

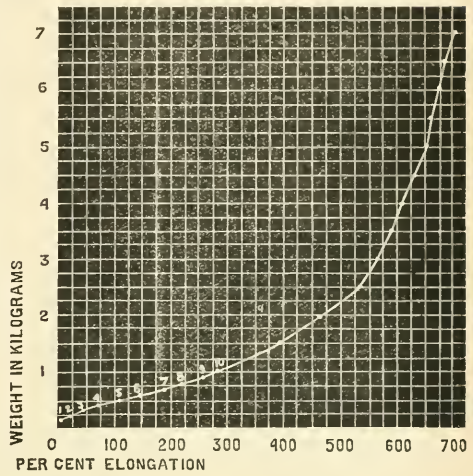
Table III.—*Tests on Vulcanised Hard-cure Para.*

Vulcanisation reference number.		Sulphur, per cent.	Tensile strength, in grms.		Elongation at rupture when original = 1·0.		Elongation under a strain of 1500 grms. when original = 1·0.	
95			2788	3164	12·2	12·5	9·2	8·7
97	U	6	3541		12·8		8·3	
114			2646	2808	13·3	12·8	10·1	9·9
115	Y	6	2970		12·4		9·8	
124	S	6	3118	3118	12·9	12·9	9·3	9·3
Mean of all tests			3013		12·7		9·3	

It will be seen that the average tensile strength of five vulcanisations, comprising three mixings, in all of which 6 per cent sulphur was used, averages 3013 grms. and the elongation 12·7 per cent. Both figures are somewhat lower than those obtained with the plantation rubber. The figures, too, are more irregular. It is far from our intention to draw rigorous conclusions from these series of tests, and we do not infer that caoutchouc in the plantation para is superior to that in the Amazonian hard cure para merely because in an average of a number of tests we have obtained slightly better figures with the former. It should be remembered that a certain treatment in mixing and vulcanising which would bring out the best qualities of plantation rubber might require some modification when applied to the hard cure product. On the other hand, we have avoided such objections as far as possible by varying the conditions, such as the duration and temperature, of vulcanisation so as to bring out the best results in both cases.

A considerable amount of work on these lines is in progress, and we hope before long to be in position to publish the results of further tests; we think, however, that with the results so far obtained we are justified in concluding that the rubber of the plantation products will prove to be at least as good if not superior to that of the Amazonian product. So far, we find that the statements frequently made in some quarters that plantation rubber is wanting in "nerve" is not justified by tests we have made on the vulcanised product obtained from the best prepared block.

We have examined the distensibility of vulcanised plantation rubber under increasing strain, and the results are plotted in the form of a curve (see Fig.).



As in the tensile strength tests, a sheet of rubber 1 mm. thick was cut in the form of a ring 40 mm. in diameter and 2·5 mm. wide. It was stretched vertically between smooth iron hooks, the upper one being fixed and the lower one carrying a scale pan. Two marks were made on the band, and the distance between them measured as weights were put into the pan.

We have also made some preliminary tests on sheets of block rubber containing mineral matter, two of which we give below. Mixing M consisted of 50 grms. caoutchouc, 4 grms. sulphur, 10 grms. zinc oxide, 25 grms. lithopone, and 1 grm. pitch; that is, approximately,—

Caoutchouc	56 per cent
Zinc oxide	11 „
Lithopone	28 „
Pitch	1 „

and sulphur, 8 per cent, reckoned on the caoutchouc.

Mixing J consisted of 50 grms. of plantation block caoutchouc, 5 grms. sulphide of antimony, and 2 grms. sulphur. The results obtained are given in Table IV.

Table IV.—*Tests on Plantation Rubbers, prepared from "Block," containing Mineral Matter.*

Vulcanisation reference number.	Mixing.	Tensile strength, in grms.	Elongation at rupture, per cent	Elongation under a strain of 1500 grms.
58	M	4746	9·9	6·0
54	J	3915	11·7	6·1

The addition of mineral matter has had the effect of increasing the tensile strength while reducing the elongation. This effect is quite general within certain limits, and further tests are being carried out in which we are investigating the influence of definite quantities of mineral matters on mixings containing plantation block on the one hand and hard-cure para on the other.

ON THE COLOUR REACTIONS OF THE LIGNO-CELLULOSES.*

By C. F. CROSS, E. J. BEVAN, and J. F. BRIGGS.

Of the many characteristic colour reactions of the ligno-celluloses, two have attracted particular attention as the basis of methods of quantitative estimations of mechanical wood-pulp as a constituent of papers. These two reactions—(*a*) with phloroglucol in presence of HCl, and (*b*) with dimethyl *p*-phenylene diamine—are in obvious contrast, and are typical of groups of reactions with phenols and with aromatic bases respectively.

We have found these reactions of service in localising reactive groups of the ligno-celluloses, and generally in pursuing our investigations of these complex plant products.

As a preliminary, we have found it necessary to further investigate the reactions themselves, to determine—(*a*) whether they are characteristic of the lignone complex strictly speaking, or (*b*) of by-products.

We have previously shown (*Journ. Chem. Soc.*, 1899, lxxv., 752) shown that the latter hypothesis is probable as regards the colour reaction with phloroglucol and other phenols, and have given some evidence for ascribing them to the presence of hydroxy-furfurals in the ligno-celluloses Compounds of this series appear to be normal by-products of spontaneous changes which they undergo in contact with atmospheric air and moisture. By the present investigation this basis of interpretation is strengthened, and our results lead to the following particular conclusions :—

(a) *Phloroglucol Reactions.*

There is a main reaction as between the ligno-cellulose and the phenol which is quantitative in character and is independent of the colour reactions.

This colour reaction is due to an associated by-product, and represents only the effect of a fraction of the total phenol combining synthetically.

(b) *Reactions with Bases.*

These reactions are not in the same sense quantitative in character, but the degree of reaction is a function of the conditions of reaction, similarly to the reactions of the ligno celluloses in combining with colouring matters.

Incidentally, we have devised experimental methods which will be found to facilitate the investigation of the constitutional problems presented by this group of "natural" products.

Interaction of Phloroglucol and Ligno-cellulose.

The general character of this reaction is shown by the following comparative experiments :—

Equal quantities of mechanical wood pulp were treated—(1) with 1 per cent of the phenol: (2) with 10 per cent of the phenol in presence of hydrochloric acid (10 per cent HCl).

After sixteen hours' digestion, the products were examined :—In (1) the phloroglucol was entirely removed from the solution ; in (2) the phenol was in excess. Notwithstanding this, the intensity of colour development was stronger in 1 than in 2.

After washing exhaustively, drying, and weighing, the excess of weight of 2 over 1 was found to be 3·5 per cent. due to the further combination with the phenol ; therefore the total weight of phloroglucol taken up in combination was 4·5 per cent, neglecting the water split off in reaction.

The following conclusions may be drawn from the observations :—There are two reactions, (*a*) with the production of a coloured body—the limit of this reaction is reached with a proportion of the phenol less than 1 per cent of the ligno-cellulose ; (*b*) a further combination with the phenol to form a compound which resists washing with water.

In order to determine the maximum absorption of the phenol, we have adapted the well-known reactions of phloroglucol with furfural in the presence of 12 per cent hydrochloric acid to a simple volumetric method, using standard test solutions of concentration 0·4 to 0·5 per cent, and carrying out the reactions at 70° C.

We find that mechanical wood pulp is a very sensitive indicator, being visibly stained by phloroglucol in solution of 1 to 30,000.

In the details of this method we have taken advantage of the exhaustive research of E. Krober in the *Journ. Landwirthschaft* (1901, p. 379).

As this method will be found of interest in technical investigations, we are communicating a special descriptive note to a technical journal (*Chemiker Zeitung*, xxxi., 725). It is sufficient to note here that it enabled us rapidly to estimate the phenol within the limits 0·5 per cent of the quantity used in our experiments.

Employing this method we avoid larger errors due to the losses of weight of the ligno-celluloses under treatment with the reagents, followed by exhaustive washing, and we are able to determine the actual maximum absorption of the phenol from solution. The following numbers have been determined :—

	Maximum absorption of phloroglucol. Per cent of Faserstoff.
Mechanical wood pulp	6·71, 6·63,
Jute	4·23, 4·20, 4·34
Wood cellulose (sulphite) ..	0·75
Esparto cellulose	0·50
Cotton cellulose	0·20

On the basis of these numbers it is clear that a quantitative technical method for the estimation of mechanical wood pulp in papers is provided, which is free from the errors inevitably associated with a colorimetric process. But the method is also of use in investigating constitutional problems ; thus we may cite observations upon two derivatives of a well characterised ligno-cellulose, the jute fibre substance, as under :—

	Absorption of phloroglucol. Per cent derivative.	Per cent original.
Jute, fully chlorinated (by combination with 8 per cent Cl)	3·9	4·0
Jute, acetylated (to 29 per cent increase of weight)	3·5	4·54

(No colour reaction in either case).

We infer from these results that chlorination produces no important change of constitution in the lignone complex, nor does the process of acetylation. But the disappearance of the colour reaction is in accordance with the view that this is due to a by-product of the furfural series which would react with the acetyl residue by its aldehydic CO group.

The evidence so far obtained goes to show that the main reaction with phloroglucol is, in fact, a reaction of synthesis with the typical quininoid groups of the lignone. It is important to note that it bears no relation to the proportion of furfural-yielding constituents of the ligno-cellulose.

In relation to the groups of celluloses and their differences the numbers obtained for esparto and wood cellulose would be influenced by residues of the lignone constituents.

Since by hydrolysis the celluloses are partially resolved with liberation of aldehydic CO groups, measured by cupric reduction methods (C. G. Schwalbe, *Ber.*, 1907, xl., 1347), we included two typical extreme "hydro-celluloses" prepared by the action of HCl (gas), as below.

	Maximum absorption of phloroglucol.
Hydro-cellulose (cotton)	0·42
Hydroligno-cellulose (jute)	4·45

* Original communicated to the *Berichte*.

The increases over the normal thus resulting have no relation to the very large increase of the free aldehydic CO groups.

It should be noted in reference to this point that the CO groups of the sugar aldehydes require a different set of conditions for reaction with productiou of insoluble products of condensation (C. Councler, *Ber.*, xxviii., 24).

Reactions of Bases with Ligno-cellulose.

Aniline and its homologues give well-marked colour reactions with the ligno-celluloses. These reactions are modified by the introduction of negative substituting groups; thus, the nitranilines give deep red colorations, and *p*-nitraniline has recently been proposed as giving more characteristic reactions (Wheeler, *Ber.*, 1907, 1888).

With the diamines there are equally characteristic colorations, and the best known of these reactions is that obtained with dimethyl-*p*-phenylenediamine. Wurster in his original papers refers the reaction to the active oxygen present in ligno-celluloses (*Ber.*, xix., 3217; xx., 808). It is evident that this effect is one of several factors of a complex result, as, indeed, has been recognised by Wurster in later publications (*Journ. Soc. Chem. Ind.*, 1903, xxii., 824).

We have made a quantitative examination of the reaction with the dimethyl base to determine its general character, making observations on the depth of colour developed in combination.

Four quantities of pine-wood meal, 1 grm. each air-dry, were treated with 0·005, 0·01, 0·02, and 0·05 grm. respectively, of dimethyl-*p*-phenylenediamine hydrochloride, each portion being dissolved in 20 cc. of 5 per cent sodium acetate solution. A fifth portion of 1 grm. was included in the series as a blank, since the woods retain nitrogenous constituents. The intensity of the colour was proportional to the quantity of base employed.

After sixteen hours, all the liquids still contained excess of the base, and gave a reaction with ligno-cellulose proportional to the quantity of base originally employed.

The product was thoroughly washed with water, and the nitrogen in the coloured product was estimated without previous drying.

The following numbers were determined, deducting in each case the nitrogen estimated in the "blank":—

Percentage of hydrochloride taken per cent of ligno-cellulose	Nitrogen fixed in combination, per cent.	Equivalent of dimethyl-*p*-phenylenediamine.
0·5	0·028	0·14
1·0	0·056	0·28
2·0	0·112	0·56
5·0	0·490	2·45

These percentages, if calculated to the anhydrous ligno-cellulose, must be increased in the ratio 90 : 100.

From these results it appears that the reactions of the ligno-celluloses with these bases are not, in the first instance, reactions with the ligno-cellulose proper; but with the aldehydic by-products or groups tending to assume the aldehydic configuration.

The quantitative features of the reactions are those which obtain rather in dyeing processes; that is, the baths are not exhausted, and the final distribution of the base, as between the ligno-celluloses and the solution, represents an equilibrium determined in part by concentration and attendant physical conditions.

Phenylhydrazine.

The reactions with this base are of the same general character, but in the first instance there is a complete absorption by combination. This is illustrated by the following numbers:—

Phenylhydrazine taken per cent of ligno-cellulose.	Phenylhydrazine absorbed.
0·5	0·5
1·0	0·9
2·0	1·6
5·0	2·5

The aldehydic constituents involved in these reactions appear to be the same as those which react with phloroglucin with development of colour.

In confirmation of this the ligno-cellulose after treatment with phenylhydrazine give no colour reaction with phloroglucin until after prolonged digestion with the acid solution of the phenol, and as a result of the gradual decomposition of the hydrazone.

It may be mentioned, though evident *à priori*, that the products of synthesis with phenylhydrazine, presumably hydrazones, are more resistant than the compounds with monamine and diamine bases, which are readily resolved by hydrolytic agents, acid and basic; the phloroglucides, on the other hand, are very resistant. They are not resolved by boiling with dilute alkalis.

This is in accordance with the quantitative relations disclosed by our results.

Hydroxylamine.

The ligno-celluloses react with this base with change of colour, which may be generally described as a partial bleaching.

We have not yet investigated those reactions quantitatively, but we may record the observation that their combination with this base entirely prevents the colour reactions with aniline and the diamines.

The reaction with phloroglucol is retarded, but after a period of digestion with the acid reagent the characteristic full development of colour is obtained.

It is evident, therefore, that the phloroglucides are well characterised derivatives, and enable us to fix the more reactive groups of the lignone complex; we hope thereby to be be able to study certain decompositions into proximate products without the complications which have hitherto rendered this a matter of exceptional difficulty.

In a later communication we shall give the results of our further investigations of the constitution of the ligno-celluloses.

THE

BALANCING OF IONIC CHEMICAL EQUATIONS.

By WILLIAM JAY KARSLAKE.

Chemical processes can be written in the form of equations in which substances are represented by their chemical symbols and formulæ. The balancing of a chemical equation then consists in finding those numerical factors called coefficients, by which each symbol and formula must be multiplied in order that the proper proportions will be expressed between the various initial and final substances involved in the change.

In making out chemical equations considerable trouble is sometimes experienced in determining the exact coefficients to be used, and therefore various devices and methods for balancing them have come into use. The principal methods for balancing ordinary chemical equations are:—

1. *The Tentative or Trial Method*, which consists in inspecting the equation and trying various coefficients until the proper ones are found.

2. *The Partial Equation Method*, which is an arithmetical device whereby the final equation is obtained through the summation of a series of partial equations.

3. *The Dualistic or Anhydride Method*, a relic of the old dualistic system of Berzelius, in which all oxygen compounds are written in the form of a positive and a negative part, as a basic and acidic oxide, and it is these various parts which are regarded as undergoing chemical change.

4. *The Algebraic Method* (James Bottomley, Chemical News, 1878, xxxvii., 110), wherein the method of indeterminate coefficients is applied, and the numerical value of the coefficients found by solving a set of simultaneous equations.

5. *The Hydride Hydroxide Method* (Ostwald's "Principles of Inorganic Chemistry," translated by Alex. Findlay,

2nd Edition, p. 607), whereby the coefficients are obtained by regarding the interacting substances as derived from those particular hydrides and hydroxides obtained by adding the elements of water to certain hydrogen and oxygen compounds of the substances under consideration.

6. *The Method of Positive and Negative Bonds* (O. C. Johnson, CHEMICAL NEWS, 1880, xlii., 51; Prescott and Johnson, "Qualitative Chemical Analysis," 5th Edition, p. 238), according to which "the number of bonds changed in one molecule of each shows the number of molecules of the other which must be taken, the words 'each' and 'other' referring to the oxidising and reducing agents" which are mutually interacting upon each other. The term "bond" as here used represents the unit of valence *actively* exhibited by the element at the time of considera tion, and is counted as a relatively positive or negative quantity according to circumstances.

While some of these methods are of value for the solution of ordinary empirical equations, most of them fail to furnish the means of solving an equation when written in the ionic or partly ionic form. This failure arises in part from the fact that in many cases the electrical charges on the ions are not accounted for, and any ionic equation to be correct must be so written that the interacting system is shown to remain electrically neutral; that is, equal quantities of positive and negative electricity must simultaneously appear or disappear in such a manner that there is no change in the sum total of the electrical charges in the system. The correct weight-ratios, therefore, between the initial and final substances involved in any ionic chemical change can only be had—(1) when the law of the conservation of weight holds good, as in ordinary equations; and (2) when the algebraic sum of the initial electrical charges is equal to that of the final electrical charges.

Aside from the tentative or trial method and the method of obtaining them from their corresponding empirical equations, there seems to be no recorded method to serve, as a rule, for the systematic balancing of ionic equations (see Talbot and Blanchard, "The Electrolytic Dissociation Theory," Chapter IV.). Yet the so-called "bond method" cited above may be extended so as to serve quite as well for the balancing of ionic equations as it does for empirical equations. To this end it is only necessary (1) to include the term "ion" under that of "molecule"; (2) to observe that while the sum of the positive and negative bonds of the atoms forming a *molecule* is zero, the sum of those forming an *ion* is equal to the valence of that ion as expressed by the number and sign of its electrical charges; (3) to count hydrogen in chemical combination as always possessing one positive bond, oxygen as possessing two negative bonds, and free elements as having no bonds; and (4) to bear in mind the necessary condition of electrical neutrality which holds for all ionic changes. As thus extended the rule for balancing ionic, partly ionic, or empirical equations may be stated as follows:—(1) The number of bonds changed in one molecule or ion of the substance oxidised shows the number of molecules or ions of the substance reduced, and *vice versâ*; and (2) the difference between the algebraic sum of the initial and final electrical charges of the partially balanced equation shows the number of molecules or ions of the remaining substances entering into the reaction, if any, which must be taken.

A few equations will illustrate the application of the method as thus extended. Reactions typical of the various kinds of ionic chemical processes in oxidation and reduction will be selected.

$$5Fe^{\cdot\cdot} + MnO_4' + 8H^{\cdot} = 5Fe^{\cdot\cdot\cdot} + Mn^{\cdot\cdot} + 4H_2O \quad . \quad . \quad 1.$$

This equation expresses the oxidation of diferrion, $Fe^{\cdot\cdot}$, by permanganion, MnO_4', in the presence of hydrion, $H^{\cdot}$. (For the system of ionic nomenclature, see James Walker, CHEMICAL NEWS, 1901, lxxxiv., 162). Here the iron in one molecule of diferrion, $Fe^{\cdot\cdot}$, gains one positive bond in passing to triferrion, $Fe^{\cdot\cdot\cdot}$; hence the number of molecules of permanganion, MnO_4', which must be taken is 1. And since all of the manganese in permanganion passes to dimanganesion, $Mn^{\cdot\cdot}$, the latter must also have a coefficient of 1. Again, since the four oxygen atoms in one molecule of permanganion, MnO_4', have a total of eight negative bonds, the manganese must have seven positive bonds, of which five are lost in passing to dimanganesion, $Mn^{\cdot\cdot}$. Hence, five molecules of diferrion are oxidised to the corresponding number of molecules of triferrion. Further, the algebraic sum of the ionic electrical charges in the final system is $+17$; therefore hydrion, $H^{\cdot}$, must be given a coefficient of 8 in order that the sum of the total ionic charges in the initial system be the same. From this it follows that the water formed has a coefficient of 4.

$$Cr_2O_7'' + 6I' + 14H^{\cdot} = 2Cr^{\cdot\cdot\cdot} + 3I_2 + 7H_2O \quad . \quad . \quad 2.$$

This equation represents the reduction of dichromanion, Cr_2O_7'', by iodidion, I', in the presence of hydrion, $H^{\cdot}$. The total chromium in one molecule of dichromanion has twelve positive bonds, and it loses six of them in passing to trichromion, $2Cr^{\cdot\cdot\cdot}$. Hence, six molecules of iodidion are oxidised to three molecules of free iodine when written as in the equation. On the other hand, the iodine in one molecule of iodidion, I', in passing to the form of free iodine, I_2 loses only one negative bond, which is equivalent to gaining one positive bond, and, consequently, the coefficient of the dichromanion is 1 and that of the trichromion formed is 2. The algebraic sum of the electric charges in the final system, the water and the free iodine being neutral, is $+6$, and in order that the initial system may have the same electrical content the coefficient of the hydrion, $H^{\cdot}$, must be 14. Hence, the water formed has a coefficient of 7.

$$2SO_3'' + 2Br_2 + 2H_2O = 2SO_4'' + 4Br' + 4H^{\cdot} \quad . \quad . \quad 3.$$

This equation represents the oxidation of sulphosion, SO_3'', to sulphanion, SO_4'', by means of bromine water. The sulphur in the sulphosion in passing to that in the sulphanion gains two positive bonds, thus reducing two molecules of free bromine to form, as written, four molecules of bromidion, Br'. The total bromine in one molecule of free bromine, Br_2, gains two negative bonds, which is equivalent to losing two positive bonds, and, consequently, 2 is the coefficient of the sulphosion which is oxidised. Further, since the sum of the ionic electrical charges in the initial system is -4, bromine and water being neutral, it follows that the hydrion, $H^{\cdot}$, formed in the final system, must have a coefficient of 4, and from this the water in the initial system must have a coefficient of 2.

$$2Fe^{\cdot\cdot\cdot} + Sn^{\cdot\cdot} = 2Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot} \quad . \quad . \quad . \quad . \quad 4.$$

This equation represents the interaction of triferrion, $Fe^{\cdot\cdot\cdot}$, and distannion, $Sn^{\cdot\cdot}$, to form diferrion, $Fe^{\cdot\cdot}$, and tetrastannion, $Sn^{\cdot\cdot\cdot\cdot}$. Here the iron in passing from triferrion to diferrion loses one positive bond, while the tin in passing from distannion to tetrastannion gains two bonds. This gives 1 for the coefficient of the distannion and 2 for that of the triferrion. The coefficients of the products formed are evident. This type of reaction illustrates the reduction or oxidation of one simple ion by another.

$$3Cu + 8H^{\cdot} + 2NO_3' = 3Cu^{\cdot\cdot} + 2NO + 4H_2O \quad . \quad . \quad 5.$$

This equation represents the action of dilute nitric acid upon metallic copper. The free copper is oxidised to dicuprion, $Cu^{\cdot\cdot}$, thus gaining two positive bonds; hence, 2 is the coefficient of the nitranion, NO_3'. On the other hand, the nitrogen in one molecule of the nitranion in passing to the form of nitric oxide loses three positive bonds; hence, three molecules of metallic copper are oxidised. Since the sum of the ionic electrical charges of the final system is $+6$ it follows that 8 must be the coefficient of the hydrion, $H^{\cdot}$, in order that the initial system may have the proper number of charges. Since all of the hydrion passes to the form of water the coefficient of the water formed must be 4.

$$Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2 \quad . \quad . \quad . \quad . \quad . \quad 6.$$

This equation represents the action of hydrion upon metallic zinc. It is an oxidation and reduction reaction, the zinc gaining two bonds in being oxidised to zincion, $Zn^{\cdot\cdot}$, while the hydrion loses one bond in being reduced to free hydrogen. Hence the coefficients are 2 and 1 as written. This reaction is typical of the preparation of hydrogen by the action of acids upon metals in general. It is also typical of the oxidation and reduction of many free substances by ionic substances, such as, for example, the precipitation of metallic copper from aqueous solutions of its salts by means of metallic zinc, $Cu^{\cdot\cdot} + Zn = Cu + Zn^{\cdot\cdot}$, or the liberation of bromine from aqueous solutions of bromides by means of free chlorine, $2Br' + Cl_2 = Br_2 + 2Cl'$, &c.

University of Iowa, Iowa City, Iowa.

INCANDESCENT ILLUMINANTS.*

By JAMES SWINBURNE, F.R.S., &c.

A LITTLE more than twenty years ago, Auer von Welsbach, who was engaged on researches on the rare earths, invented the modern incandescent mantle. His first mantles were made of zirconia and yttrite earth, in the proportion to make a normal zirconate. Shortly afterwards, he found that the best material has a basis of thoria. Pure thoria, which requires care in its preparation, gives very little light, but if a small percentage of a coloured and permanent oxide, such as ceria, is added, it gives good illumination.

There has been much discussion about the theory of the incandescent mantle. It has been generally assumed that the temperature of a Bunsen burner is too low for a mantle to give the light it does by simple radiation, unless it is much hotter than the flame. Unfortunately, the temperature of the flame is generally taken with a thermo-couple, and this gives far too low a reading, as the thermo-couple never reaches the real temperature of the flame. But, admitting that the temperature of the flame is high, it is still urged that the light given by the thoria with a small percentage of ceria is so great that there is something else than mere thermal radiation. It is said that the ceria acts as a catalytic agent, and that it oscillates between two states of oxidation. Ceria does act in somewhat the same way as platinum; for instance, if a ceria mantle is put on a lighted burner, and the burner turned out, and the gas turned on again, the ceria mantle will glow and will finally light the gas. It is odd that this is not brought forward by the advocates of the catalysis theory; but the opponents might urge that zirconia will do the same thing, and the zirconia mantle gives very little light. This does not really dispose of the catalytic theory.

According to the simple radiation theory, the light depends only on the emissivity, or blackness of the mantle, and its temperature. Its temperature must be lower than the flame, as it must be robbing the flame of the heat it radiates. In order to give the flame every chance of supplying the heat, the threads of the mantle have to be made very fine, so that the flame can rush through the meshes, and the hot gas should be in brisk movement through the interstices of the mantle. By using a special draught arrangement, known as the intensive system, about twice the light per cubic foot of gas can be obtained. In order to get the highest temperature the emissivity should be low, that is to say, the mantle should be very white; but then, though it would get to a high temperature, it would give very little light. On increasing the emissivity the light will first increase, but this means a lower temperature, so that as the emissivity is increased from white to black, the total radiation increases, but as that means a greater abstraction of heat from the flame, the mantle is cooler, and therefore radiates a larger proportion of the energy as heat and a smaller proportion as light, so the mantle gets redder and gives less light. This is just what happens in practice, whether ceria or any other coloured oxide is used.

It has been urged that as pure ceria is white, adding it cannot make the mantle blacker; but ceria is white only when cold. A mantle may look quite white cold, and be darker in colour when hot. Rubens has devised an experiment to show this. The mantle is strongly illuminated by an arc and condenser, and its image is thrown on the screen. It looks quite white, of course. On lighting the gas, the mantle, instead of becoming still brighter, at once becomes dull. Again, alumina, which is white, gives little light. Chromium oxide is so dark that it gives only a dull red glow. But on adding a little chromium oxide to the alumina, a dark red light is first given, because the chromium oxide is too dark; but as soon as it combines with the alumina to make a light pink mantle, a good light is obtained.

The incandescent mantle is now applied not only to the ordinary Bunsen burner, but to an inverted form, which lends itself to decoration, and to the petroleum lamp. It is now also applied to air carrying a little hydrocarbon gas, and this application is said to provide an extraordinarily cheap light, which is especially useful for country houses.

One of the drawbacks of gas, compared with electric lighting, is that merely turning on does not light gas. This difficulty has been largely overcome by the use of the by-pass, but further advances have been made. Welsbach has discovered that an alloy of cerium and iron gives off sparks on being scraped or filed, and a burner has been designed in which the act of turning on the gas scrapes a little wheel of this alloy, causing a spark, which lights the gas. This overcomes the drawback of having a little jet always burning. Another invention allows the gas to be lighted from a main tap. Each burner has an attachment, which lets the gas straight through to the burner when the pressure is on; but on turning the main supply off, and allowing a little gas to pass at the controlling tap, the attachment to each burner turns off the burner and lights a little pilot jet, which keeps alight until the light is wanted again. On turning on the main tap, the pilot jets light the various burners and go out themselves. By this means burners can be fully lighted up by turning one tap at the door of the room.

The electric incandescent light is undergoing a great change. Carbon is being replaced by metal wires. It has been found possible to make wires of high enough resistance of tungsten, osmium, tantalum, and a few other metals and compounds. The osmium lamp was the first of these, but there was difficulty in making it of high enough resistance. The tantalum lamp is now in great demand. It is made for 100 to 130 volts, and is much more efficient than the carbon lamp. It will not last long on alternating currents, however. The wires of a lamp that have been run for some time on a direct current show a curious notched or crinkled appearance under the microscope. But a wire that has been run on an alternating circuit looks as if the metal had been melted into short cylinders with round ends, and these cylinders had stuck together end to end without their centres being in a line. Sometimes the little cylinders are nearly separated, merely touching at a corner. This action is very extraordinary, and has never been explained. In addition to this, when a lamp breaks down on an alternating circuit, the wire sometimes goes at one point, and sometimes it breaks in several places, and tangles itself up in an extraordinary way; at other times it breaks up into numerous little pieces, which will be found lying on the inside of the globe. Some of the other lamps show a change under the action of the current, but it is not so marked as in the case of tantalum.

One of the most interesting of the new lamps is the Zircon. It is said to be made of zirconium and tungsten, and lamps of this material have been made for 200 volts, a matter of the greatest importance from a distribution point of view. It is possible that the conductor is really a

* Abstract of a Discourse delivered at the Royal Institution, April 26, 1907.

zirconide of tungsten, and this opens up a new series of compounds. A Zircon lamp for 100 volts has really six separate loops of wire mounted in series inside a bulb. A recent improvement is to provide an extremely light spring for each loop, so as to keep it taut. The lamp can then be used in any position.

Tungsten seems to be the favourite metal, as it gives a very high efficiency. It is probable the lamp of the future will have an efficiency of nearly a candle per watt, and this is promised by the use of tungsten. At the same time it must be admitted that to make a wire with a resistance of 500 ohms small enough to give 20 candles with 20 watts is a triumph of inventive skill.

The lecture was illustrated by numerous experiments.

THE USE OF SUCCINIC ACID AS A STANDARD IN ALKALIMETRY AND ACIDIMETRY.

By I. K. PHELPS and J. L. HUBBARD.

Succinic acid as a standard in alkalimetry and acidimetry has had an extended use for some time. We are not aware that the best methods of preparation of pure material for such a purpose, or the limits of accuracy of succinic acid in such a procedure, have been recorded. We give in detail below work concerning these points.

To determine the strength of the solution of ammonium hydroxide used in this work in neutralising definite weights of succinic acid, a solution of hydrochloric acid approximately *n*/10, was made up by diluting in the usual way with distilled water pure hydrochloric acid. The solution of hydrochloric acid was standardised by precipitating in a volume of 250 cc. definite portions of it held in a platinum dish with silver nitrate in excess in presence of a few drops of nitric acid, filtering off the precipitate, allowed to stand twenty-four hours, after cooling to zero centigrade to remove from solution traces of silver chloride (W. A. Roth, *Zeit. f. Angew. Chem.*, xvii., 716), filtering off on asbestos under pressure in a perforated platinum crucible, rinsing with water cooled to zero, drying at 100° C., and weighing after cooling in a desiccator. The solution of ammonium hydroxide was titrated against the solution of hydrochloric acid, using tincture of cochineal as the indicator, and by diluting with distilled water in suitable amounts was made of such strength that 1 cc. corresponded exactly to 1 cc. of the hydrochloric acid solution.

Succinic acid was prepared in four different ways—by the hydrolysis of the pure ester, by hydration of the pure anhydride, by crystallisation of the acid from a solution of the succinic acid of commerce in hot water, and by crystallisation of the acid from the solution of the acid of commerce in hot water containing nitric acid.

From purified succinic ester, boiling at 213·3—213·5° C. under a barometric pressure of 749 mm., pure succinic acid was obtained by boiling it for four hours on a return condenser with nitric acid and water in these proportions—20 cc. of succinic ester, 200 cc. of water, three drops of nitric acid. This solution was evaporated to crystallisation, and, after filtering off from the mother-liquor, the solid product was re-crystallised from distilled water. These crystals were dried carefully in the open air to constant weight, and it was found that on standing over sulphuric acid in a desiccator this weight remained unchanged. By this procedure the purest succinic acid melting in an open capillary tube at 182·3° C. was obtained.

For the preparation of the acid from succinic anhydride the anhydride was purified by re-crystallising from absolute alcohol until the crystals obtained after carefully drying melted sharply at 119° C. The pure anhydride obtained in this manner was converted to the acid by dissolving it in distilled water heated to the boiling-point, filtering off the crystals formed on cooling the solution, and drying. It was found that these crystals, as in the case of the succinic acid crystals described above, came to constant weight when dried in the air, and that this weight remained unchanged when the product was allowed to stand in a desiccator over sulphuric acid. Samples made in this way melted at 182·8° C. in an open capilliary tube.

Preparations of succinic acid were made from the acid of commerce by dissolving the latter in distilled water at the boiling-point, crystallising by cooling and drying in the air. No loss in weight was found when the air-dried material was exposed in the desiccator. It melted in an open capillary tube at 181·7° C.

The acid was also made by dissolving the succinic acid of commerce in boiling water, adding nitric acid, crystallising, and drying the crystals thus obtained. In this manner a product of a slightly higher degree of purity was obtained than that crystallised from water. This product melted in an open capilliary tube 182·3° C.

TABLE I.

No.	Succinic acid.	HCl corresponding to succinic acid— Found.	Theory.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0·2000	0·1231	0·1235	0·0004 –
2.	0·2000	0·1231	0·1235	0·0004 –
3.	0·2000	0·1231	0·1235	0·0004 –
4.	0·2000	0·1231	0·1235	0·0004 –
5.	0·2000	0·1231	0·1235	0·0004 –
6.	0·2000	0·1231	0·1235	0·0004 –
7.	0·2000	0·1233	0·1235	0·0002 –
8.	0·2000	0·1233	0·1235	0·0002 –
9.	0·2000	0·1231	0·1235	0·0004 –
10.	0·2000	0·1233	0·1235	0·0002 –
11.	0·2000	0·1234	0·1235	0·0001 –
12.	0·2000	0·1234	0·1235	0·0001 –
13.	0·2000	0·1235	0·1235	0·0000
14.	0·2000	0·1235	0·1235	0·0000
15.	0·2000	0·1235	0·1235	0·0000
16.	0·2000	0·1235	0·1235	0·0000

In all of the experiments recorded in the table definite portions of succinic acid were dissolved in distilled water, and into the solution the ammonium hydroxide of definite strength was drawn carefully from a burette until the succinic acid was exactly neutralised as shown by the cochineal tincture used to indicate the completion of the reaction. The experiments were conducted so that the final volume in each case was about 250 cc. at the completion of neutralisation of the succinic acid. The succinic acid used in Experiments 1, 2, 3, and 4 recorded in the table was that obtained by crystallising the succinic acid of commerce from water at the boiling-point, and dried in the air. The material in 5 and 6 was the same product crystallised from water, and dried in a desiccator. In Experiments 7 and 8 the succinic acid used was that purified by crystallising from hot water with a few drops of nitric acid. In Experiments 9, 10, 11, and 12 the succinic acid used was made from the purified anhydride, dried to constant weight in the air. The material used in Experiments 13, 14, 15, and 16 was the succinic acid prepared by hydrolysing the pure succinic ester boiling at 213·3—213·5° C.

It is clear from the work shown in the table that succinic acid may serve admirably as a standard for work in alkalimetry and acidimetry. It is further obvious that for such work succinic acid of a fair degree of purity may be prepared by crystallising the acid of commerce from water at the boiling-point, or preferably by crystallising from water at the boiling-point containing nitric acid. The product obtained by the hydration of the anhydride is of an excellent state of purity. Succinic acid of ideal constitution may be prepared by hydrolysing the pure ester. While in every case air drying of the samples is sufficient, drying in a desiccator over sulphuric acid involves no risk of the formation of the anhydride.

Since succinic ester in a state of purity may be prepared with ease, succinic acid is conveniently available as a standard in alkalimetry and acidimetry. It is equally reliable with the previously most valued standard—hydrochloric acid standardised gravimetrically as silver chloride. —*American Journal of Science*, xxiii., p. 211.

SOME ASTRONIMICAL CONSEQUENCES OF THE PRESSURE OF LIGHT.*

By Professor J. H. POYNTING, Sc.D. F.R.S.

The experiments of Lebedew and Nichols and Hull have proved conclusively that light presses against any surface upon which it falls, and the extraordinarily accurate experiments of Nichols and Hull have fully confirmed Maxwell's calculation that the pressure per square centimetre is equal to the energy in the beam per cubic centimetre.

A clearer idea of the effect of light or radiation pressure is obtained by thinking of a beam of light as a carrier of momentum. We then see that not only does it press against a receiving surface, but also against the surface from which it started.

Some experiments by Dr. Barlow and myself appear to bring to the front this conception of light as a momentum carrier. If a beam falls on a black surface at an angle to the normal, there should be a tangential stress along the surface. An experiment was described in which light fell on a blackened disc at the end of a torsion arm, the disc being at right angles to the arm (*Phil. Mag.*, 1905, ix., p. 169). The disc was pushed round by the tangential stress. The experiment was carried out in a partially exhausted vessel, but the residual air was a source of disturbance by convection and radiometer effects. A better experiment was made by suspending a disc of mica blackened beneath, about 2 inches in diameter by a quartz fibre, the disc being horizontal and suspended from its centre. When a beam of light fell at 45° on a part of the disc, the horizontal component of the beam being at right angles to the radius to the part where it fell, the disc moved round through the combined effects of convection, radiometer action, and the tangential stress. When the beam was allowed to fall on the same place at 45° on the other side of the vertical, convection and radiometer action were very nearly as before, but the tangential stress was reversed. The difference in torsion in the two cases was twice that due to the tangential stress. An experiment with prisms (*Ibid.*, p. 403) was also described.

Regarding a beam of light as a momentum carrier, it is easily seen that if the receiving surface has velocity u towards the source and the velocity of light is U, the pressure is increased by the motion by the fraction u/U. If the velocity is reversed, the pressure is decreased by this fraction. This is the "Doppler reception effect."

If the source is moving, and we assume that the amplitude of the emitted waves depends on the temperature and nature of the source alone, it can be shown that the pressure on the source is $U/(U+u)$ of its value when the source is at rest. This is the "Doppler emission effect."

In considering the consequence of light pressure, it is necessary to know the temperature of a body exposed to the sun's radiation. It can be shown that a small black particle, at the distance of the earth from the sun, has about the mean temperature of the earth's surface, say 300° Abs., and that the temperature of the sun is about twenty times as high, say 6000 Abs. The temperature of the particle varies inversely as the square root of its distance from the sun.

The direct pressure of sunlight is virtually a lessening of the sun's gravitation pull. On bodies of large size this is negligible. On the earth it is only about a forty billionth of the sun's pull, but the ratio increases as the diameter decreases, and a particle one forty-billionth of the earth's diameter, and of the same density, would be pushed back as much as it is pulled in, if the law held good down to such a size. If the radiating body is diminished, the ratio of gravitation pull to light push is similarly diminished, and it can be shown that two bodies of the temperature of the earth's surface and of the earth's mean density would neither attract nor repel each other, if their diameter was about 1 inch. The consequence of this on a swarm of meteorites is obvious. It is probable that this balancing of gravitation and light pressure must be taken into account in the motion of the particles supposed to constitute Saturn's rings.

When we consider the motion of a small particle round the sun, we have, first, the direct pressure lessening gravitation. If it has density equal to that of the earth and diameter 1/1000 inch, the lessened pull at the distance of the earth will imply a lengthening of the year by nearly two days. Secondly, the Doppler emission effect comes into play, for the particle crowds forward on its own waves emitted in front, and draws away from those emitted behind, so that there is increase of pressure in front and a decrease behind. Thus there is a force resisting the motion. The particle will then tend to fall inwards in its orbit, and in the case considered about 800 miles in the first year. It would probably move in a spiral into the sun, and reach it in less than 100,000 years. A particle 1 inch in diameter would reach the sun from the earth in less than a hundred million years. The Doppler reception effect will not come into play in a circular orbit, but in an elliptic orbit it acts as if it were a force resisting change of distance, and therefore it tends to make an elliptic orbit even more circular.

Applying these considerations to a comet regarded as a swarm of small particles coming into our system, a sorting action will at once begin. The smaller particles will have their period of revolution lengthened out more than the larger ones, and they will tend to trail behind. The Doppler emission effect will damp down the motion, and again, more markedly with the smaller particles, and all will tend to spiral into the sun. The Doppler reception effect will tend to destroy the ellipticity of the orbit, more especially with the smaller particles, and ultimately the particles of different sizes may move in orbits so different that they may not appear to belong to the same system. In course of time they should all end in the sun. Perhaps the zodiacal light is due to the dust of long dead comets.

It appears just possible that Saturn's rings may be cometary matter which the planet has captured, and on which these actions have been at play for so long that the orbits have become circular.

* Abstract of a Discourse delivered at the Royal Institution, May 11, 1906.

NOTICES OF BOOKS.

Investigations of the Theory of the Photographic Process. By S. E. Sheppard, D.Sc. (Lond.), and C. E. Kenneth Mees, D.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

The authors of this discussion of the theory of the photographic process have applied physico-chemical methods to the study of development, fixation, &c., and have to record some important results thereby obtained. They have, as far as possible, performed all experiments quantitatively, and the numerical results are in all cases given in full, while the references to authoritative text-books and original articles, and the short historical accounts of each division of the subject, show that they have made every endeavour to provide as comprehensive a view of the whole theory of photographic work as possible. In the chapters on the sensitometry of photographic plates an attempt is made to add to the value of the plate as an instrument of research by determining the relation between the light employed

and the effect produced, and a short account is given of the colour sensitiveness of plates; this last chapter having been left unaltered since it was written now over a year ago, the latest work that has been done by Callier and by Belin on the subject could not be described, but the authors have evidently devised reliable methods of investigating an important question from a quantitative point of view.

A Text-book of Electro-chemistry. By MAX LE BLANC. Translated by WILLIS R. WHITNEY, Ph.D., and JOHN W. BROWN, Ph.D. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1907.

THE new translation from the fourth German edition of this text-book constitutes the second English edition, in which, although the earlier version has been freely used, many important additions and alterations have been made. A new feature is the adoption of a consistent notation throughout the book; in it the various symbols are used as far as possible in the same sense as in other important works on physical and electro-chemistry, and although its use will perhaps be found a little troublesome at first, the student working systematically through the book will no doubt very soon get accustomed to it, while the reader, who is merely referring to the book for special information, will in many cases understand it readily if he is acquainted with chemical or electrical literature, and it is explained in full in an appendix. The text-book has been much used in England, and no doubt the new edition will be well received. It gives on the whole a satisfactory survey of theoretical and general electro-chemistry, though in some respects the author's treatment of important branches of the subject is rather scanty. For instance, the relation between chemical constitution and conductivity might with advantage be considered more fully, while the importance of Lorenz's work on the conduction of fused salts would warrant more than an allusion to it in a foot-note only, more especially as much research work on the subject is waiting to be done.

The Chemistry and Technology of Mixed Paints. By MAXIMILLIAN TOCH. New York: D. Van Nostrand Company. London: Crosby Lockwood and Son. 1907.

THIS book is original in conception and working out, and brings before the reader some fresh aspects of the chemistry of paints. It is the first work devoted exclusively to the subject of mixed paints which has yet appeared, and not unnaturally it exhibits the defects which often mar pioneering work, while at the same time it puts new problems before the paint chemist, and opens up a wide field of research. Much of the text is devoted to a description of the author's investigations, and chemists who have had a good general training in analysis will find that many of the author's suggestions for experimental work might, if followed up, lead to important technical developments. In the first part of the book the manufacture of mixed paints is described, with some account of the chemistry of the raw materials, in which the author has omitted much information which is to be found in the usual text-books, and has thus made room for the results of his experiences upon various points of interest or dispute. The chapters on paint vehicles are marked by the same originality and independence of conclusions generally accepted, as shown, for instance, in the section on China Wood Oil, the use of which is frequently condemned, though without due cause in the author's opinion. On the analysis of mixed paints some notes are given, but the subject is not treated sufficiently systematically to make the section of any real use except to an expert already familiar with the general methods employed. In fact the whole character of the book is such that, while it contains much that will be of value as a supplement which throws an interesting light upon recent research, it could not be adopted as a text-book for students who were beginning the study of paint chemistry.

The Textile Fibres. By J. MERRITT MATTHEWS, Ph.D., Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

THIS text-book of the physical, microscopical, and chemical properties of the textile fibres is a valuable addition to the literature of the subject, and should be studied from cover to cover by all students of Textile Schools. The author has taken into account the needs of manufacturers, and pays considerable attention to practice, so that the book throws light upon many of the problems which are likely to confront those engaged in the industry. From a scientific point of view the work will be found most stimulating, and as the chemical nature of the fibres has as yet been but little investigated, the worker who uses the book will find that he is not likely to want a profitable subject for research. Many micrographs by the author add to the value of the text, and the laboratory methods used in the qualitative and quantitative analysis of the fibres are fully described, while the comprehensive scheme for the examination of different fibres will be found a valuable practical aid to the student.

Das Werden der Welten. ("The Development of the Worlds"). By SVANTE ARRHENIUS. Translated from the Swedish by L. BAMBERGER. Leipzig: Akademische Verlagsgesellschaft, m.b.H. 1907.

THIS exposition of Prof. Arrhenius's views upon many disputed questions in cosmic physics will receive the careful attention of students of astronomy and of the problems of the cosmos. The fruitfulness of the great Swedish chemist's theories in general chemistry will no doubt influence the minds of many of his readers as to their acceptance of some of his daring assumptions, provided that they are not too rigidly bound by convention, and it goes without saying that he clothes his views in most stimulating language. The central idea of the book is that the world was always essentially the same as it now is, and that matter, energy, and life have only changed form and position in space. Upon this theme he writes with enthusiasm and inspiration, and astronomers and cosmic physicists will find that the book well repays careful study. In particular, emphasis is laid upon the theory of the pressure of radiation, which opens up a wide field of enquiry, and special attention is called to Lebedew's pioneering work, which is generally speaking somewhat neglected. Possibly the parts of the book which will be most interesting to the general reader are those which deal with the appearance of life upon this planet, on which subject the author has some new suggestions to make.

Die Kathodenstrahlen. ("Cathode Rays"). By G. C. SCHMIDT. Braunschweig: Friedrich Vieweg und Sohn. 1907.

THE importance of the possession of an adequate knowledge of the essentials of the electron theory by all who are engaged in scientific work of any description is fully recognised, and this book will consequently receive a hearty welcome on all sides. It contains a clear account of the discovery and properties of the cathode rays, and shows how the electron theory is based upon them. The outlines of the theory are put forward in the simplest possible way, mathematical discussions being omitted as far as possible, and no reader need fear that his scientific knowledge is insufficient to enable him to understand the main purport of the book. Very little previous acquaintance with natural phenomena is assumed; thus the book opens with a chapter on the undulatory theory of light and the nature of the ether, and throughout Prof. Schmidt shows a marked power of insight into the difficulties the new conceptions are likely to present to those who are reading of them for the first time, while his language is admirably suited to dispel these diffi-

culties and to arouse the fullest interest of the reader. The book is divided into short chapters, each of which introduces some new important fact or theory, which is presented in such a way that every advance is thoroughly defined and explored before the next is made, which is a valuable feature from the point of view of the elementary reader.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 25, June 24, 1907.

New Method of Preparing Anhydrous Lithium Oxide.—M. de Forcrand.—Li_2O can be prepared by the dissociation of the carbonate at 780—800° in a current of dry hydrogen, as well as by the dehydration of the hydrate. The author has determined the heat of solution of Li_2O (30 grms.) in 4 litres of water at 15° and obtains the number 31·200 cals., which differs very considerably from that stated by Beketoff. The degree of dilution has a great influence upon the heat of solution, and Li_2O previously dissolved in 4 litres evolves 0·306 cal. when the liquid is diluted to 15 litres. In this respect lithium resembles the metals of the alkaline earths and differs from the alkali metals. The heat of solution also depends upon the temperature, increasing by about 0·098 cal. for every degree.

Hydration of Ethylene Oxides.—Louis Henry.—Epichlorhydrine, $ClCH_2{-}CH{-}CH_2$ (O bridge), when subjected to the action of sulphuric acid gives the primary glyceric monochlorhydrine, $ClCH_2{-}CH(OH){-}CH_2(OH)$, and all ethylene compounds containing the group $>C{-}C<$ (O bridge) resemble it in this respect. This reaction can be employed practically for the preparation of the ethylene glycols, $>C(OH){-}C(OH)<$. Thus, if the oxide of isobutylene, $(CH_3)=C{-}CH_2$ (O bridge), is introduced into water and dilute sulphuric acid is added, heat is evolved, and, after cooling, the glycol can be separated from the liquid by means of potassium carbonate. This glycol is isobutylenic glycol, $(CH_3)_2=C(OH){-}CH_2OH$. When oxides richer in carbon are treated in the same way less heat is evolved. Thus oxides containing the group $>C{-}C<$ (O bridge) differ from the glycolic oxides such as—

$CH_2{-}(CH_2)_2CH_2$ (O bridge) or $CH_3{-}CH{-}(CH_2){-}CH{-}CH_3$ (O bridge),

which are not affected by sulphuric acid.

Sulphammonium.—P. Lebeau and P. Damoiseau.—In 1905 Ruff and Geisel stated that the action of sulphur upon ammonia may be represented by the reversible equation $10S+16NH_3 \rightleftharpoons N_4S_4+6(NH_4)_2S$, and that the coloration of sulphammonium is produced only in presence of free sulphur, which gives a colloidal solution with the liquefied ammonia. To establish this fact they endeavoured to show the presence of sulphuretted hydrogen and nitrogen sulphide in sulphammonium. However, as a trace of an impurity is often sufficient to bring about a reaction, the authors thought that a trace of water—which is difficult to avoid in the case of a gas as hygroscopic as ammonia—might play some part in the reaction. They therefore repeated the experiments, taking special precautions to ensure the absence of moisture, and then found that Ruff and Geisel's reversible reaction does not represent the true facts unless water is present; and, moreover, their observations on the stability and the identity of the coloration of solutions of sulphammonium containing very different proportions of sulphur and ammonia, show that Moissan's conclusions regarding the existence of sulphammonium as a type of ammonium compound are not disproved.

Compounds of Silicon and Molybdenum. Molybdenum Disilicide.—Ed. Defacqz.—When a mixture of copper silicide and amorphous molybdenum (obtained by the reduction of the oxide by hydrogen at a red heat) is heated in the electric furnace, grey crystals of a silicide of molybdenum having the formula Si_2Mo are obtained. The density of the compound is 6·2 at 0°; it is non-magnetic. It is attacked by chlorine at 350—400°, giving silicon tetrachloride and molybdenum pentachloride. Aqua regia containing hydrofluoric acid dissolves it easily when heated with it on a water-bath, giving a clear liquid from which a residue of molybdic acid is obtained upon evaporation. Soda, potash, and alkaline carbonates convert it into a mixture of silicate and alkaline molybdate. Boiling hydrochloric acid, nitric acid, and sulphuric acid have no action upon it.

Different Molecular States of Anhydrous and Hydrated Ferric Sulphate.—A. Recoura.—The author has already described three varieties of ferric sulphate with very different properties, one of them anhydrous, and the others isomeric hydrates: $Fe_2O_3.3SO_3.9H_2O$ (yellow and white). When the white hydrated sulphate is kept at a temperature a little below 100° it loses six molecules of water. If the temperature is then raised to 175° the dehydration is complete, but the yellowish brown anhydrous compound differs from the ordinary anhydrous sulphate in that it dissolves in water in a few minutes. When exposed to moist air also it behaves differently, being hydrated much more rapidly, and giving neither the yellow nor the white sulphate, but a third hydrated variety, which is also obtained by keeping the white hydrated sulphate at a temperature below 100°. It differs from the other two hydrated sulphates in that it dissolves very rapidly in alcohol (in about one hour). These five hydrates are not the only ones that exist; the action of heat on the yellow hydrated sulphate yields other varieties.

Cuprous Iodide.—Marcel Guichard.—If dry hydriodic acid is passed over anhydrous cuprous chloride at the ordinary temperature, heat is evolved and some iodine is liberated. If the product of the reaction is evaporated *in vacuo* at 40°, the free iodine sublimes and a white substance, cuprous iodide, remains behind. When prepared in the wet way by the action of alkaline iodides or hydriodic acid upon cupric salts in solution, cuprous iodide, whether dried at a low temperature or at 130°, retains a small quantity of water (much less than a molecule), which it gives up only with difficulty. When heated in air, even below 200°, it oxidises, losing iodine, but *in vacuo* at about 300° dehydration is complete. When it is heated *in vacuo* it turns yellow, and fuses to a brown liquid at 600°, and on cooling passes back through the same changes of colour to a white solid. The author analysed the compound by heating it in air and weighing the copper oxide and iodine thus formed, and obtained results which agree very closely with those calculated for anhydrous cuprous iodide.

Alloys of Cobalt and Tin.—F. Ducelliez.—The author has prepared alloys of cobalt and tin by heating the two metals in a current of hydrogen in a Schlœsing furnace. The alloys obtained are very different in appearance according to the amount of tin they contain. When the amount present is above 85 per cent they resemble tin and can be cut; below 85 per cent they are hard and brittle. If alloys containing 80 to 92 per cent of tin are treated with nitric acid and boiled, then the residue is treated with metastannic

acid, and the residue from this process treated with fused potash and washed, a grey metallic powder is obtained which has the formula $CoSn$. Its density is 8·95 at 0°. Chlorine and oxygen both attack it, and sulphur vapour gives fused sulphides at a red heat. Hydrochloric acid and sulphuric acid completely dissolve it, but dilute nitric acid has no effect, even when boiled; hot concentrated nitric acid and alkaline carbonates act slowly upon it, and alkaline nitrates and potassium chlorate oxidise it with difficulty.

A Molybdo-uranium Compound.—André Lancien.—When ammonium molybdate acts on uranyl nitrate a precipitate is formed which has the composition corresponding to the formula $MoO_4.UrO_2$, and is therefore a molybdate of uranyl. The yield is theoretical, and in the dark an amorphous white powder is obtained. It is insoluble in water, ethyl and methyl alcohol, acetic acid, chloroform, benzene, toluene, and sulphuric ether. Ethyl and methyl alcohol and acetic acid transform it into a green uranous compound. When boiled for a long time with the bases NH_3, KOH, NaOH it turns brick-red, and then gives a green oxide. It dissolves quickly in HCl, H_2SO_4, HNO_3, $H_2S_2O_7$. Its physical and chemical properties appear to change after it has been kept for thirty hours; it is then yellow in colour, insoluble in HNO_3, and not reduced by ethyl alcohol. It is a radio-active substance, and its activity is about equal to that of barium bromide, and much superior to that of uranyl nitrate.

Lupeol.—E. Jungfleisch and H. Leroux.—From the guttapercha of *Palaquium Treubi* the authors have isolated a cinnamic ether which is identical with the cinnamate of lupeol. In the course of their experiments they found that lupeol when heated loses water, giving a hydrocarbon, which may be called lupeylene. The analysis of lupeol, its cinnamate, and lupeylene, led to the formula $C_{30}H_{50}O$ for the alcohol, which is that of a monovalent alcohol, derived from a triterpene; the alcohol derivatives of the terpenes, the isocamphenols, when heated readily give a hydrocarbon and water, thus resembling lupeol. The fact that the action of bromine upon lupeol has led to different results in the hands of different observers is to be explained by this transformation into water and hydrocarbon.

Action of Ethereal Salts of α-Iodo Fatty Acids upon Phenylamine Magnesium Iodide and Ortho-toluidine Magnesium Iodine.—F. Bodroux and F. Taboury.—Ethyl iodo-acetate reacts normally on ortho-toluidine magnesium iodide (in solution), but has practically no action upon phenylamine magnesium iodide (precipitated). The authors thought that this difference was due to the physical states in which the organo-magnesium compound was employed, and repeated the experiment with phenylamine magnesium iodide, using enough ethyl oxide to keep the organo-metallic substance in solution. It was then found that iodo-acetanilide was formed.

$$CH_2I{-}COOC_2H_5 + 2C_6H_5{-}NH{-}Mg{-}I =$$
$$= CH_2I{-}C(O{-}Mg{-}I)(NH{-}C_6H_5)(NH{-}C_6H_5) + Mg(OC_2H_5)I.$$

$$CH_2I{-}C(O{-}Mg{-}I)(NH{-}C_6H_5)(NH{-}C_6H_5) + 2HCl =$$
$$= Mg(Cl)I + C_6H_5{-}NH_2{-}HCl + CH_2I{-}CO{-}NH{-}C_6H_5.$$

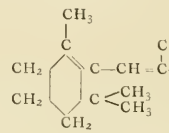
Similarly, when ethyl α-iodo propionate and butyrate are used, the corresponding compounds, *e.g.*, $CH_3{-}CHI{-}CO{-}NH{-}C_6H_5$, &c., are obtained. These compounds are solids, crystallising in white needles, and slowly turning yellow under the influence of light.

Origin of Deposits of Colouring Matter in Red Wines.—A. Trillat.—Pasteur has shown that red wine when protected from the air can be kept indefinitely without any deposit being formed, but when the wine is exposed to the air the colouring matter is oxidised and a deposit is formed. The author has proved that the colouring matter of red wine whem dissolved in a dilute acid in absence of alcohol can be kept for a long time in contact with oxygen without undergoing any change, while the addition of aldehyde produces a precipitate. The further examination of this point shows that the conversion of the alcohol of wine into aldehyde is one of the causes, if not the principal cause, of the formation of the deposits.

Synthesis of an Aldehyde with an Odour of Violets.—Ph. Barbier.—Citral condenses with propanol, giving a mixture of two isomers with the formula $C_{13}H_{26}O$. The structural formula of the first isomer, which boils at 147—148° under 13 mm., is—

$$CH_3{-}C(CH_3){=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CH{-}C(CH_3){-}CHO,$$

and it is thus an unsaturated aldehyde. When dissolved in sulphuric acid, heated to 50° or 60°, and cooled, two isomers of the cyclic aldehyde—



are obtained. These aldehydes have a strong odour of fresh violets. They oxidise very readily in air, and cannot therefore be used as a substitute for ionone, to which they are greatly superior in odour.

MISCELLANEOUS.

City and Guilds of London Institute.—At a meeting of the Council of the City and Guilds of London Institute held on the 22nd inst. it was resolved to confer the Fellowship of the Institute (F.C.G.I.) upon Mr. Alfred E. Young, A.C.G.I., A.M.I.C.E., F.R.A.S., F.R.G.S., Chief Surveyor of the Federated Malay States, for his original and valuable work in the Trigonometrical Survey of the Malay States. Mr. Young matriculated at the City and Guilds Central Technical College in 1877, he obtained the John Samuel Scholarship at the end of 1889, and was awarded the Diploma of "Associate" of the Institute in 1890.

Institute of Chemistry.—*Pass List of the July Examinations*, 1907.—Of twenty-eight candidates who entered for the Intermediate Examination, the following twenty-two passed: N. C. Akers, A. D. Black, J. Boyd, J. Brebner, M.A., B.Sc. (Aberdeen), R. Bruce, A. M. Cameron, B.Sc. (Edin.), H. R. Cooper, B.Sc. (Lond.), F. G. Crosse, W. C. Davis, M. C. Fletcher, H. L. Gammon, J. Gibbon, N. McN. Hyslop, R. D. Masson, R. L. Morris, J. W. H. Pattison, A. S. Petrie, O. D. Roberts, W. F. Russell, A. Sandeman, P. A. W. Self, B.Sc. (Lond.), and Miss Maggie Millen Jeffs Sutherland. In the Final Examination for the Associateship (A.I.C.), of five examined in the Branch of Mineral Chemistry, three passed: William Garsed, William Godden, Assoc.R.C.Sc. (Lond.), B.Sc. (Lond.), and Eric Hayward. Of two examined in the Branch of Metallurgical Chemistry, one passed: E. B. Naylor, M.Sc. (Manchester). Of five examined in Organic Chemistry, three passed: F. Baker, B.Sc. (Lond.), J. H. Lane, and B. D. W. Luff. Of seven (including one Associate) who entered in the Branch of the Analysis of Food and Drugs and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following four passed: R. R. Bennett, F. M. Dyke, B.Sc. (Lond.), W. R. S. Ladell, and D. J. Law, B.Sc. (Lond.).

THE CHEMICAL NEWS.

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BRITISH ASSOCIATION
FOR THE
ADVANCEMENT OF SCIENCE.

Leicester, 1907.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir David Gill, K.C.B., LL.D., D.Sc., F.R.S., Hon. F.R.S.E., &c.

To-night, for the first time in its history, the British Association meets in the ancient city of Leicester; and it now becomes my privilege to convey to you, Mr. Mayor, and to the citizens generally, an expression of our thanks for your kind invitation and for the hospitable reception which you have accorded to us.

Here in Leicester and last year in York, the Association has followed its usual custom of holding its annual meeting somewhere in the United Kingdom; but in 1905 the meeting was, as you know, held in South Africa. Now, having myself only recently come from the Cape, I wish to take this opportunity of saying that this southern visit of the Association has, in my opinion, been productive of much good; wider interest in science has been created amongst colonists, juster estimates of the country and its problems have been formed on the part of the visitors, and personal friendships and interchange of ideas between thinking men in South Africa and at home have arisen which cannot fail to have a beneficial influence on the social, political, and scientific relations between these colonies and the mother country. We may confidently look for like results from the proposed visit of the Association to Canada in 1909.

One is tempted to take advantage of the wide publicity given to words from this chair to speak at large in the cause of science, to insist upon the necessity for its wider inclusion in the education of our youth and the devotion of a larger measure of the public funds in aid of scientific research; to point to the supreme value of science as a means for the culture of those faculties which in man promote that knowledge which is power; and to show how dependent is the progress of a nation upon its scientific attainment.

But in recent years these truths have been prominently brought before the Association from this Chair; they have been exhaustively demonstrated by Sir William Huggins from the Chair of the Royal Society, and now a special guild (the British Science Guild) exists for their enforcement upon the mind of the nation.

These considerations appear to warrant me in following the healthy custom of so many previous Presidents, viz., of confining their remarks mainly to those departments of science with which the labours of their lives have been chiefly associated.

The Science of Measurement.

Lord Kelvin in 1871 made a statement from the Presidential Chair of the Association at Edinburgh as follows:—"Accurate and minute measurement seems to the non-scientific imagination a less lofty and dignified work than the looking for something new. But nearly all the grandest discoveries of science have been the reward of accurate measurement and patient long-continued labour in the minute sifting of numerical results."

Besides the instances quoted by Lord Kelvin in support of that statement, we have perhaps as remarkable and typical an exemplification as any in Lord Rayleigh's long-continued work on the density of nitrogen which led him to the discovery of argon. We shall see presently that, true as Lord Kelvin's words are in regard to most fields of science, they are especially applicable as a guide in astronomy.

One of Clerk Maxwell's lectures in the Natural Philosophy Class at Marischall College, Aberdeen, when I was a student under him there, in the year 1859, ran somewhat as follows:—

> A standard, as it is at present understood in England, is not a real standard at all; it is a rod of metal with lines ruled upon it to mark the yard, and it is kept somewhere in the House of Commons. If the House of Commons catches fire there may be an end of your standard. A copy of a standard can never be a real standard, because all the work of human hands is liable to error. Besides, will your so-called standard remain of a constant length? It certainly will change by temperature, it probably will change by age (that is, by the rearrangement or settling down of its component molecules), and I am not sure if it does not change according to the azimuth in which it is used. At all events, you must see that it is a very impractical standard—impractical because if, for example, any one of you went to Mars or Jupiter, and the people there asked you what was your standard of measure, you could not tell them, you could not reproduce it, and you would feel very foolish. Whereas, if you told any capable physicist in Mars or Jupiter that you used some natural invariable standard, such as the wave-length of the D line of sodium vapour, he would be able to reproduce your yard or your inch, provided that you could tell him how many of such wave-lengths there were in your yard or your inch, and your standard would be available anywhere in the universe where sodium is found.

That was the whimsical way in which Clerk Maxwell used to impress great principles upon us. We all laughed before we understood; then some of us understood and remembered.

Now the scientific world has practically adopted Maxwell's form of natural standard. It is true that it names that standard the metre; but that standard is not one-millionth of the Earth's quadrant in length, as it was intended to be; it is merely a certain piece of metal approximately of that length.

It is true that the length of that piece of metal has been reproduced with more precision, and is known with higher accuracy in terms of many secondary standards, than is the length of any other standard in the world; but it is, after all, liable to destruction and to possible secular change of length. For these reasons it cannot be scientifically described otherwise than as a piece of metal whose length at 0° C. at the epoch A.D. 1906 is = 1,553,164 times the wave-length of the red line of the spectrum of cadmium when the latter is observed in dry air at the temperature of 15° C. of the normal hydrogen-scale at a pressure of 760 mm. of mercury at 0° C.

This determination, recently made by methods based on the interference of light-waves and carried out by MM. Perot and Fabry at the International Bureau of Weights and Measures, constitutes a real advance in scientific metrology. The result appears to be reliable within one ten-millionth part of the metre.

The length of the metre, in terms of the wave-length of the red line in the spectrum of cadmium, had been determined in 1892 by Michelson's method, with a mean result in almost exact accordance with that just quoted for the comparisons of 1906; but this agreement (within one part in ten millions) is due in some degree to chance, as the uncertainty of the earlier determination was probably ten times greater than the difference between the two independent results of 1892 and 1906.

We owe to M. Guillaume, of the same International Bureau, the discovery of the remarkable properties of the

alloys of nickel and steel, and from the point of view of exact measurement the specially valuable discovery of the properties of that alloy which we now call "invar." He has developed methods for treatment of wires made from this alloy which render more permanent the arrangement of their constituent molecules. Thus these wires, with their attached scales, may, for considerable periods of time and under circumstances of careful treatment, be regarded as nearly invariable standards. With proper precautions, we have found at the Cape of Good Hope that these wires can be used for the measurement of base lines of the highest geodetic precision with all the accuracy attainable by the older and most costly forms of apparatus; whilst with the new apparatus a base of 20 kilometres can be measured in less time and far less cost than one of a single kilometre with the older forms of measurement.

The Great African Arc of Meridian.

In connection with the progress of geodesy, time only permits me to say a few words about the Great African arc on the 30th meridian, which it is a dream of my life to see completed.

The gap in the arc between the Limpopo and the previously executed triangulation in Rhodesia, which I reported to the Association at the Johannesburg meeting in 1905, has now been filled up. My own efforts, at 6000 miles distance, had failed to obtain the necessary funds, but at Sir George Darwin's instance contributions were obtained from this Association, from the Royal Society and others, to the extent of half the estimated cost; the remaining half was met by the British South Africa Company. But for Darwin's happy intervention, which enabled me to secure the services of Captain Gordon and his party before the Transvaal Survey Organisation was entirely broken up, this serious gap in the great work would probably have long remained; for it is one thing to add to an existing undertaking of the kind, it is quite another to create a new organisation for a limited piece of work.

Since then Colonel (now Sir William) Morris has brought to a conclusion the reductions of the geodetic survey of the Transvaal and Orange River Colony, and his report is now in my hands for publication.

Dr. Rubin, under my direction, at the cost of the British South Africa Company, has carried the arc of meridian northwards to S. latitude 9° 42′, so that we have now continuous triangulation from Cape L'Agulhas to within fifty miles of the southern end of Lake Tanganyika; that is to say, a continuous geodetic survey extending over twenty-five degrees of latitude.

It happens that, for the adjustment of the international boundary between the British Protectorate and the Congo Free State, a topographic survey is at the present moment being executed northward along the 30th meridian from the northern border of German East Africa. A proposal on the part of the Royal Society, the Royal Geographical Society, the British Association, and the Royal Astronomical Society has been made to strengthen this work by carrying a geodetic triangulation through it along the 30th meridian, and thus adding 2½° to the African arc. These Societies together guarantee £1000 towards the cost of the work, and ask for a like sum from Government to complete the estimated cost. The topographic survey will serve as the necessary reconnaisance. The topographic work will be completed by the end of January next, and the four following months offer the best season of the year for geodetic operations in these regions.

There is a staff of skilled officers and men on the spot sufficient to complete the work within the period mentioned, and the Intercolonial Council of the Transvaal and Orange River Colony most generously offers to lend the necessary geodetic instruments. The work will have to be done sooner or later, but if another expedition has to be organised for the purpose the work will then cost from twice to three times the present amount. One cannot therefore doubt that His Majesty's Government will take advantage of the present offer and opportunity to vote the small sum required. This done, we cannot doubt that the German Government will complete the chain along the eastern side of Lake Tanganyika, which lies entirely within their territory. Indeed, it is no secret that the Berlin Academy of Sciences has already prepared the necessary estimates with a view to recommending action on the part of its Government.

Captain Lyons, who is at the head of the survey of Egypt, assures me that preliminary operations towards carrying the arc southwards from Alexandria have been begun, and we have perfect confidence that in his energetic hands the work will be prosecuted with vigour. In any case the completion of the African arc will rest largely in his hands. That arc, if ever my dream is realised, will extend from Cape L'Agulhas to Cairo, thence round the eastern shore of the Mediterranean and the islands of Greece, and there meet the triangulation of Greece itself, the latter being already connected with Struve's great arc, which terminates at the North Cape in lat. 70° N. This will constitute an arc of 105° in length—the longest arc of meridian that is measurable on the earth's surface.

The Solar Parallax.

Much progress has been made in the exact measurement of the great fundamental unit of astronomy—the solar parallax.

Early in 1877 I ventured to predict that we should not arrive at any certainty as to the true value of the solar parallax from observations of transits of Venus, but that the modern heliometer applied to the measurement of angular distances between stars and the star-like images of minor planets would yield results of far higher precision ("The Determination of the Solar Parallax," *The Observatory*, vol. i., p. 280).

The results of the observations of the minor planets Iris, Victoria, and Sappho at their favourable oppositions in the years 1888 and 1889, which were made with the co-operation of the chief heliometer and meridian observatories, fully justified this prediction (*Annals of the Cape Observatory*, vol. vi., Part 6, p. 29). The Sun's distance is now almost certainly known within one-thousandth part of its amount. The same series of observations also yielded a very reliable determination of the mass of the Moon.

The more recently discovered planet Eros, which in 1900 approached the Earth within one-third of the mean distance of the Sun, afforded a most unexpected and welcome opportunity for re-determining the solar parallax—an opportunity which was largely taken advantage of by the principal observatories of the northern hemisphere. Unfortunately the high northern declination of the planet prevented its observation at the Cape and other southern observatories. So far as the results have been reduced and published they give an almost exact accordance with the value of the solar parallax derived from the heliometer observations of the minor planets, Iris, Victoria, and Sappho in 1888 and 1889 (see *Monthly Notices R.A.S.*, Hinks, vol. lxiv., p. 725; Christie, vol. lxvii., p. 382).

But in 1931 Eros will approach the Earth within one-sixth part of the Sun's mean distance, and the fault will rest with astronomers of that day if they do not succeed in determining the solar parallax within one ten-thousandth part of its amount.

To some of us who struggled so hard to arrive at a tenth part of this accuracy under the less favourable geometrical conditions that were available before the discovery of Eros, how enviable seems the opportunity!

And yet, if we come to think of it rightly, the true opportunity and the chief responsibility is ours, for *now* and not twenty years hence is the time to begin our preparation; *now* is the time to study the origin of those systematic errors which undoubtedly attach to some of our photographic processes; and then we ought to construct telescopes specially designed for the work. These telescopes should be applied to the charting of the stars near

the path which Eros will describe at its opposition in 1931, and the resulting star-co-ordinates derived from the plates photographed by the different telescopes should be rigorously intercompared. Then, if all the telescopes give identical results for the star-places, we can be certain that they will record without systematic error the position of Eros. If they do not give identical results, the source of the errors must be traced.

The planet will describe such a long path in the sky during the opposition of 1931 that it is already time to begin the meridian observations which are necessary to determine the places of the stars that are to be used for determining the constants of the plates. It is desirable, therefore, that some agreement should be come to with respect to selection of these reference stars, in order that all the principal meridian observatories in the world may take part in observing them.

I venture to suggest that a Congress of Astronomers should assemble in 1908 to consider what steps should be taken with reference to the important opposition of Eros in 1931.

The Stellar Universe.

And now to pass from consideration of the dimensions of our solar system to the study of the stars, or other suns, that surround us.

To the lay mind it is difficult to convey a due appreciation of the value and importance of star-catalogues of precision. As a rule such catalogues have nothing whatever to do with discovery in the ordinary sense of the word, for the existence of the stars which they contain is generally well known beforehand; and yet such catalogues are, in reality, by far the most valuable assets of astronomical research.

If it be desired to demarcate a boundary on the Earth's surface by astronomical methods, or to fix the position of any object in the heavens, it is to the accurate star catalogue that we must refer for the necessary data. In that case the stars may be said to resemble the trigonometrical points of a survey, and we are only concerned to know from accurate catalogues their positions in the heavens at the epoch of observation. But in another and grander sense the stars are not mere landmarks, for each has its own apparent motion in the heavens which may be due in part to the absolute motion of the star itself in space, or in part to the motion of the solar system by which our point of view of surrounding stars is changed.

If we desire to determine these motions and to ascertain something of the general conditions which produce them, if we would learn something of the dynamical conditions of the universe and something of the velocity and direction of our own solar system through space, it is to the accurate star catalogues of widely separated epochs that we must turn for a chief part of the requisite data.

The value of a star-catalogue of precision for present purposes of cosmic research varies as the square of its age and the square of its accuracy. We cannot alter the epoch of our observations, but we can increase their value fourfold by doubling their accuracy. Hence it is that many of our greater astronomers have devoted their lives chiefly to the accumulation of meridian observations of high precision, holding the view that to advance such precision is the most valuable service to science they could undertake, and comforted in their unselfish and laborious work only by the consciousness that they are preparing a solid foundation on which future astronomers may safely raise the superstructure of sound knowledge.

But since the extension of our knowledge of the system of the universe depends quite as much on past as on future research, it may be well, before determining upon a programme for the future, to consider briefly the record of meridian observation in the past for both hemispheres.

The Comparative State of Astronomy in the Northern and Southern Hemispheres.

It seems probable that the first express reference to southern constellations in known literature occurs in the Book of Job (ix. 9): "Which maketh Arcturus, Orion, and Pleiades, and the chambers of the south." Schiaparelli's strongly supported conjecture is that the expression "chambers of the south," taken with its context, signifies the brilliant stellar region from Canopus to α Centauri, which includes the Southern Cross and coincides with the most brilliant portion of the Milky Way.

About the year 750 B.C. (the probable date of the Book of Job) all these stars culminated at altitudes between 5° and 16° when viewed from the latitude of Judæa; but now, owing to precessional change, they can only be seen in a like striking manner from a latitude about 12° further south.

The words of Dante have unquestionably originated the wonderful net of poetic fancy that has been woven about the asterism, which we now call Crux.

> To the right hand I turned, and fixed my mind
> On the other pole attentive, where I saw
> Four stars ne'er seen before save by the ken
> Of our first parents—Heaven of their rays
> Seemed joyous. O thou northern site! bereft
> Indeed, and widowed, since of these deprived.

All the commentators agree that Dante here referred to the stars of the Southern Cross.

Had Dante any imperfect knowledge of the existence of these stars, any tradition of their visibility from European latitudes in remote centuries, so that he might poetically term them the stars of our first parents?

Ptolemy catalogues them as 31, 32, 33, and 34 Centauri, and they are clearly marked on the Borgian globe described by Assemanus in 1790. This globe was constructed by an Arabian in Egypt: it bears the date 622 Hegira, corresponding with A.D. 1225, and it is possible that Dante may have seen it.

Amerigo Vespucci, as he sailed in tropical seas, apparently recognised in what we now call Crux the four luminous stars of Dante; for in 1501 he claimed to be the first European to have looked upon the stars of our first parents. His fellow-voyager, Andrea Corsali, wrote about the same time to Giuliano di Medici describing "the marvellous cross, the most glorious of all the celestial signs."

Thus much mysticism and romance have been woven about this constellation, with the result that exaggerated notions of its brilliancy have been formed, and to most persons its first appearance, when viewed in southern latitudes, is disappointing.

To those, however, who view it at upper culmination for the first time from a latitude a little south of the Canary Islands, and who at the same time make unconsciously a mental allowance for the absorption of light to which one is accustomed in the less clear skies of Northern Europe, the sight of the upright cross, standing as if fixed to the horizon, is a most impressive one. I at least found it so on my first voyage to the Cape of Good Hope. But how much more strongly must it have appealed to the mystic and superstitious minds of the early navigators as they entered the unexplored seas of the northern tropic! To them it must have appeared the revered image of the Cross pointing the way on their southward course—a symbol and sign of Hope and Faith on their entry to the unknown.

The first general knowledge of the brighter stars of the southern hemisphere we owe to Frederick de Hautman, who commanded a fleet sent by the Dutch Government in 1595 to the Far East for the purpose of exploring Japan. Hautman was wrecked and taken prisoner at Sumatra, and whilst there he studied the language of the natives and made observations of the positions and magnitudes of the fixed stars of the southern hemisphere. (The resulting catalogue of 304 stars is printed as an appendix to Hautman's *Vocabulary of the Malay Language*, published at Amsterdam in 1603.)

Our distinguished countryman Halley visited St. Helena in 1677 for the purpose of cataloguing the stars of the southern hemisphere. He selected a station now marked

Halley's Mount on the Admiralty chart of the island. I have visited the site, and the foundations of the observatory still remain. Halley's observations were much hindered by cloud. On his return to England, Halley in 1679 published his "Catalogus Stellarum Australium," containing the magnitudes, latitudes, and longitudes of 341 stars, which, with the exception of seven, all belonged to the southern hemisphere.

But the first permanently valuable astronomical work in the southern hemisphere was done in 1751-52 by the Abbé de Lacaille. He selected the Cape of Good Hope as the scene of his labours, because it was then perhaps the only spot in the world situated in a considerable southern latitude which an unprotected astronomer could visit in safety, and where the necessary aid of trained artisans to erect his observatory could be obtained. Lacaille received a cordial welcome at the hands of the Dutch governor Tulbagh; he erected his observatory in Cape Town, made a catalogue of nearly 10,000 stars, observed the opposition of Mars, and measured a short arc of meridian all in the course of a single year. Through his labours the Cape of Good Hope became the birthplace of astronomy and geodesy in the southern hemisphere.

Bradley was laying the foundations of exact astronomy in the northern hemisphere at the time when Lacaille laboured at the Cape. But Bradley had superior instruments to those of Lacaille, and much longer time at his disposal. Bradley's work is now the basis on which the fair superstructure of modern astronomy of precision rests. His labours were continued by his successors at Greenwich, and by a long series of illustrious men like Piazzi, Groombridge, Bessel, Struve, and Argelander. But in the southern hemisphere the history of astronomy is a blank for seventy years from the days of Lacaille.

We owe to the establishment of the Royal Observatory at the Cape by an Order in Council of 1820 the first successful step towards the foundation of astronomy of high precision in the southern hemisphere.

Time does not permit me to trace in detail the labours of astronomers in the southern hemisphere down to the present day; and this is the less necessary because in a recent Presidential Address to the South African Philosophical Society I have given in great part that history in considerable detail (*Trans. South African Phil. Soc.*, vol. xiv., Part 2). But I have not there made adequate reference to the labours of Dr. Gould and Dr. Thome at Cordoba. To their labours, combined with the work done under Stone at the Cape, we owe the fact that for the epoch 1875 the meridian sidereal astronomy of the southern hemisphere is nearly as well provided for as that of the northern. The point I wish to make is that the facts of exact sidereal astronomy in the southern hemisphere may be regarded as dating nearly a hundred years behind those of the northern hemisphere.

The Constitution of the Universe.

It was not until 1718, when Edmund Halley, afterwards Astronomer Royal of England, read a paper before the Royal Society, entitled "Considerations on the Change of the Latitudes of some of the Principal Fixt Stars," that any definite facts were known about the constitution of the universe (*Phil. Trans.*, 1718, p. 738). In that paper Halley, who had been investigating the precession of the equinoxes, says:—"But while I was upon this enquiry I was surprized to find the Latitudes of three of the principal Stars in heaven directly to contradict the supposed greater obliquity of the Ecliptick, which seems confirmed by the Latitudes of most of the rest."

This is the first mention in history of an observed change in the relative position of the so-called fixed stars—the first recognition of what we now call "proper motion."

Tobias Mayer, in 1760, seems to have been the first to recognise that if our Sun, like other stars, has motion in space, that motion must produce apparent motion amongst the surrounding stars; for in a paper to the Göttingen Academy of Sciences he writes:—"If the Sun, and with it the planets and the Earth which we inhabit, tended to move directly towards some point in the heavens, all the stars scattered in that region would seem to gradually move apart from each other, whilst those in the opposite quarter would mutually approach each other. In the same manner one who walks in the forest sees the trees which are before him separate, and those that he leaves behind approach each other." No statement of the matter could be more clear; but Mayer with the meagre data at his disposal, came to the conclusion that "the motions of the stars are not governed by the above or any other common law, but belong to the stars themselves."

Sir William Herschel, in 1783, made the first attempt to apply, with any measure of success, Mayer's principle to a determination of the direction and amount of the solar motion in space (*Phil. Trans.*, 1783, p. 247). He derived, as well as he could from existing data, the proper motions of fourteen stars, and arrived by estimation at the conclusion that the Sun's motion in space is nearly in the direction of the star λ Herculis, and that 80 per cent of the apparent motions of the fourteen stars in question could be assigned to this common origin.

This conclusion rests in reality upon a very slight basis, but the researches of subsequent astronomers show that it was an amazing accidental approach to truth—indeed, a closer approximation than Herschel's subsequent determinations of 1805 and 1806, which rested on wider and better data (*Phil. Trans.*, 1805, p. 233; 1806, p. 205).

Consider for a moment the conditions of the problem. If all the stars except our Sun were at rest in space, then, in accordance with Mayer's statement, just quoted, all the stars would have apparent motions on great circles of the sphere away from the apex and towards the antapex of the solar motion. That is to say, if the position of each star of which the apparent motion is known was plotted on the surface of a sphere and a line with an arrow-head drawn through each star showing the direction of its motion on the sphere, then it should be possible to find a point on the sphere such that a great circle drawn from this point through any star would coincide with the line of direction of that star's proper motion. The arrow-heads would all point to that intersection of the great circles which is the antapex of the solar motion, and the other point of intersection of the great circles would be the apex; that is to say, the direction of the Sun's motion in space.

But as the apparent stellar motions are small and only determinable with a considerable percentage of error, it would be impossible to find any point on the sphere such that every great circle passing through it and any particular star, would in every case be coincident with the observed direction of motion of that star.

Such discordances would, on our original assumption, be due to errors of observation, but in reality much larger discordances will occur, which are due to the fact that the other stars (or suns) have independent motions of their own in space. This at once creates a new difficulty, viz., that of defining an absolute locus in space. The human mind may exhaust itself in the effort, but it can never solve the problem. We can imagine, for example, the position of the Sun at any moment to be defined with reference to any number of surrounding stars, but by no effort of imagination can we devise means of defining the *absolute* position of a body in space without reference to surrounding material objects. If, therefore, the referring objects have unknown motions of their own, the rigour of the definition is lost.

What we call the observed proper motion of a star has three possible sources of origin.

1. The *parallactic motion*, or the effect of our Sun's motion through space, whereby our point of view of surrounding celestial objects is changed.

2. The *peculiar* or particular motion of the star, *i.e.*, its own *absolute* motion in space.

3. That part of the observed or tabular motion which is due to inevitable error of observation.

In all discussions of the solar motion in space, from that

of Herschel down till a recent date, it has been assumed that the peculiar motions of the stars are arranged at random, and may therefore be considered zero in the mean of a considerable number of them. It is then possible to find such a value for the Precession, and such a common apex for the solar motion as shall leave the residual peculiar motions of the stars under discussion to be in the mean = zero. That is to say, we refer the motion of the Sun in space to the centre of gravity of all the stars considered in the discussion, and regard that centre of gravity as immovable in space.

In order to proceed rigorously, and especially to determine the amount as well as the direction of the Sun's motion in space, we ought to know the parallax of every star employed in the discussion, as well as its proper motion. In the absence of such data it has been usual to start from some such assumption as the following:—The stars of a particular magnitude are roughly at the same distance; those of different classes of magnitude may be derived from the hypothesis that on the average they have all equal absolute luminosity.

The assumption is not a legitimate one—

1. Because of the extreme difference in the absolute luminosity of stars.

2. Because it implies that the average absolute luminosity of stars is the same in all regions of space.

The investigation has been carried out by many successive astronomers on these lines with fairly accordant results as to the position of the solar apex, but with very unsatisfactory results as to the distances of the fixed stars (see Note). In order to judge how far the magnitude (or brightness) of a star is an index of its probable distance, we must have evidence from direct determinations of stellar parallax.

(Note.—Argelander, "Mém. présentés à l'Acad. Imp. des Sciences St. Pètersbourg," tome iii.; Lundahl, *Astron. Nachrichten*, No. 398, 209; Argelander, *Astron. Nachrichten*, No. 398, 210; Otto Struve, *Mém. Acad. des Sciences St. Pétersbourg*, Series 6, Math. et Phys., tome iii., p. 17; Galloway, *Phil. Trans.*, 1847, p. 79; Mädler, *Dorpat Observations*, vol. xiv., and *Ast. Nach.*, No. 566, 213; Airy, *Mem. R.A.S.*, vol. xxviii., p. 143; Dunkin, *Mem. R.A.S.*, vol. xxxii., p. 19; Stone, *Monthly Notices R.A.S.*, vol. xxiv., p. 36; De Ball, Inaugural Dissertation, Bonn, 1877; Rancken, *Astron. Nachrichten*, No. 2482, 149; Bischoff, Inaugural Dissertation, Bonn, 1884; Ludwig Struve, *Mém. Acad. St. Pétersbourg*, Series 7, tome xxxv., No. 3).

Stellar Parallax.

To extend exact measurement from our own solar system to that of other suns and other systems may be regarded as the supreme achievement of practical astronomy. So great are the difficulties of the problem, so minute the angles involved, that it is but in comparatively recent years that any approximate estimate could be formed of the true parallax of any fixed star. Bradley felt sure that if the star γ Draconis had a parallax of 1″ he would have detected it. Henderson by "the minute sifting of the numerical results" of his own meridian observations of α Centauri, made at the Cape of Good Hope in 1832-33, first obtained certain evidence of the measurable parallax of any fixed star. He was favoured in this discovery by the fact that the object he selected happened to be, so far as we yet know, the nearest sun to our own. Shortly afterwards Struve obtained evidence of a measurable parallax for α Lyræ and Bessel for 61 Cygni. Astronomers hailed with delight this bursting of the constraints which our imperfect means imposed on research. But for the great purposes of cosmical astronomy what we are chiefly concerned to know is not what is the parallax of this or that particular star, but rather what is the average parallax of a star having a particular magnitude and proper motion. The prospect of even an ultimate approximate attainment of this knowledge seemed remote. The star α Lyræ is one of the brightest in the heavens; the star 61 Cygni one that had the largest proper motion known at the time; whilst α_2 Centauri is not only a very bright star, but it has also a large proper motion. The parallaxes of these stars must therefore in all probability be large compared with the parallax of the average star; but yet to determine them with approximate accuracy long series of observations by the greatest astronomers and with the finest instruments of the day seemed necessary.

Subsequently various astronomers investigated the parallaxes of other stars having large proper motions, but it was only in 1881, at the Cape of Good Hope, that general research on stellar parallax was instituted (*Mem. R.A.S.*, vol. xlviii.). Subsequently, at Yale and at the Cape of Good Hope the work was continued on cosmical lines with larger and improved heliometers (*Annals of the Cape Observatory*, vol. viii., Part 2; and *Trans. Astron. Observatory of Yale University*, vol. i.). By the introduction of the reversing prism and by other practical refinements the possibilities of systematic error were eliminated, and the accidental errors of observation reduced within very small limits.

These researches brought to light the immense diversity in the absolute luminosity and velocity of motion of different stars. Take the following by way of example:—

Our nearest neighbour amongst the stars, α_2 Centauri, has a parallax of 0·76″, or is distant about 4¼ light-years. Its mass is independently known to be almost exactly equal to that of our Sun; and its spectrum being also identical with that of our Sun, we may reasonably assume that it appears to us of the same magnitude as would our Sun if removed to the distance of α_2 Centauri.

But the average star of the same apparent magnitude as α_2 Centauri was found to have a parallax of only 0·10″, so that either α_2 Centauri or our Sun, if removed to a distance equal to that of the average fixed star of the first magnitude, would appear to us but little brighter than a star of the fifth magnitude.

Again, there is a star of only 8½ magnitude (Gould's Zones, Vh 243), which has the remarkable annual proper motion of nearly 8¾ seconds of arc—one of those so-called runaway stars—which moves with a velocity of 80 miles per second at right angles to the line of sight (we no not know with what velocity in the line of sight). It is at about the same distance from us as Sirius, but it emits but one ten-thousandth part of the light energy of that brilliant star. Sirius itself emits about thirty times the light-energy of our Sun, but it in turn sinks into insignificance when compared with the giant Canopus, which emits at least 10,000 times the light-energy of our Sun.

Truly "one star differs from another star in glory." Proper motion rather than apparent brightness is the truer indication of a star's probable proximity to the Sun. Every star of considerable proper motion yet examined has proved to have a measurable parallax.

This fact at once suggests the idea, Why should not the apparent parallactic motions of the stars, as produced by the Sun's motion in space, be utilised as a means of determining stellar parallax?

Secular Parallactic Motion of Stars.

The strength of such determinations, unlike those made by the method of annual parallax, would grow with time. It is true that the process cannot be applied to the determination of the parallax of individual stars, because the peculiar motion of a particular star cannot be separated from that part of its apparent motion which is due to parallactic displacement. But what we specially want is not to ascertain the parallax of the individual star, but the mean parallax of a particular group or class of stars, and for this research the method is specially applicable, provided we may assume that the peculiar motions are distributed at random, so that they have no systematic tendency in any direction; in other words, that the centre of gravity of any extensive group of stars will remain fixed in space.

This assumption is, of course, but a working hypothesis,

and one which from the paper on star-streaming communicated by Professor Kapteyn, of Groningen, to the Johannesburg meeting of the Association two years ago we already know to be inexact (*Rep. Brit. Assoc.*, 1905, p. 257). Kapteyn's results were quite recently confirmed in a remarkable way by Eddington, using independent material discussed by a new and elegant method (*Monthly Notices R.A.S.*, vol. lxvii., p. 34). Both results showed that, at least for extensive parts of space, there are a nearly equal number of stars moving in exactly opposite directions. The assumption, then, that the mean of the peculiar motions is zero may, at least for these parts of space, be still regarded as a good working hypothesis.

Adopting an approximate position of the apex of the solar motion, Kapteyn resolved the observed proper motions of the Bradley stars into two components, viz., one in the plane of the great circle passing through the star and the apex, the other at right angles to that plane (" Publications Astron. Laboratory Groningen," Nos. 7 and 9). The former component obviously includes the whole of the parallactic motion; the latter is independent of it, and is due entirely to the real motions of the stars themselves. From the former the mean parallactic motion of the group is derived, and from the combination of the two components, the relation of velocity of the Sun's motion to that of the mean velocity of the stars of the group.

As the distance of any group of stars found by the parallactic motion is expressed as a unit in terms of the Sun's yearly motion through space, the velocity of this motion is one of the fundamental quantities to be determined. If the mean parallax of any sufficiently extensive group or class of stars was known we should have at once means for a direct determination of the velocity of the Sun's motion in space; or if, on the other hand, we can by independent methods determine the Sun's velocity, then the mean parallax of any group of stars can be determined.

Determination of Stellar Motion in the Line of Sight.

Science owes to Sir William Huggins the application of Doppler's principle to the determination of the velocity of star-motion in the line of sight. The method is now so well known, and such an admirable account of its theory and practical development was given by its distinguished inventor from this Chair at the Cardiff meeting in 1891, that further mention of that part of the matter seems unnecessary.

The Velocity of the Sun's Motion in Space.

If by this method the velocities in the line of sight of a sufficient number of stars situated near the apex and antapex of the solar motion could be determined, so that in the mean it could be assumed that their peculiar motions would disappear, we have at once a direct determination of the required velocity of the Sun's motion.

The material for this determination is gradually accumulating, and indeed much of it, already accumulated, is not yet published. But even with the comparatively scant material available, it now seems almost certain that the true value of the Sun's velocity lies between 18 and 20 kilometres per second (Kapteyn, *Ast. Nach.*, No. 3487, p. 108; and Campbell, *Astrophys. Journ.*, xiii., p. 80); or, if we adopt the mean value, 19 kilometres per second, this would correspond almost exactly with a yearly motion of the Sun through space equal to four times the distance of the Sun from the Earth.

Thus the Sun's yearly motion being four times the Sun's distance, the parallactic motion of stars in which this motion is unforeshortened must be four times their parallax. How this number varies with the amount of foreshortening is of course readily calculated. The point is that from the mean parallactic motion of a group of stars we are now enabled to derive at once its mean parallax.

This research has been carried out by Kapteyn for stars of different magnitudes. It leads to the result that the parallax of stars differing *five* magnitudes does *not* differ in the proportion of one to ten, as would follow from the supposition of equal luminosity of stars throughout the universe, but only in the proportion of about one to five (*Astron. Nachrichten*, No. 3487, Table III.; and *Ast. Journ.*, p. 566).

The same method cannot be applied to groups of stars of different proper motions, and it is only by a somewhat indirect proof, and by calling in the aid of such reliable results of direct parallax determination as we possess, that the variation of parallax with proper motion could be satisfactorily dealt with.

The Mean Parallaxes of Stars of Different Magnitude and Proper Motion.

As a final result Kapteyn derived an empirical formula giving the average parallax for stars of different spectral types, and of any given magnitude and proper motion. This formula was published at Groningen in 1901 (" Publications Astron. Laboratory Groningen, No. 88, p. 24). Within the past few months the results of researches on stellar parallax, made under the direction of Dr. Elkin, at the Astronomical Observatory of Yale University, during the past thirteen years, have been published (*Trans. Astron. Observatory of Yale University*, vol. ii. Part I.), and they afford a most crucial and entirely independent check on the soundness of Kapteyn's conclusions.

In considering the comparison between the more or less theoretical results of Kapteyn and the practical determinations of Yale, we have to remember that Kapteyn's tables refer only to the means of groups of a large number of stars having on the average a specified magnitude and proper motion, whilst the latter are direct determinations affected by the accidental errors of the separate determinations and by such uncertainty as attaches to the unknown parallaxes of the comparison stars—parallaxes which we have supplied from Kapteyn's general tables.

The Yale results consist of the determination of the parallax of 173 stars, of which only ten had been previously known to Kapteyn, and had been utilised by him. Dividing these results into groups we get the following comparison:—

Comparison Groups arranged in order of Proper Motion.

No. of stars.	Proper motion.	Magnitude.	Parallax. Yale.	Parallax. Kapteyn.	Yale—Kapteyn.
	"		"	"	"
21	0·14	3·8	0·028	0·026	+0·002
39	0·49	6·3	0·042	0·055	−0·013
45	0·59	6·7	0·068	0·060	+0·008
46	0·77	6·5	0·047	0·074	−0·027
22	1·50	6·2	0·118	0·124	−0·006
		Groups arranged in order of Magnitude.			
10	0·61	0·8	0·103	0·110	−0·007
29	0·53	3·8	0·076	0·075	+0·001
33	0·63	5·6	0·064	0·070	−0·006
34	0·73	6·7	0·055	0·070	−0·017
31	0·68	7·6	0·025	0·061	−0·036
36	0·80	8·3	0·056	0·062	−0·006
		Spectral Type I.			
13	0·42	4·0	0·076	0·076	0·000
		Spectral Type II.			
81	0·67	5·3	0·067	0·074	−0·007

These results agree in a surprisingly satisfactory way, having regard to the comparatively small number of stars in each group and the great range of parallax which we know to exist amongst individual stars having the same magnitude and proper motion. In the mean perhaps the tabular parallaxes are in a minute degree too large, but we have unquestionable proof from this comparison that our knowledge of stellar distances now rests on a solid foundation.

The Distribution of Varieties of Luminosity of Stars.

But, besides the mean parallax of stars of a particular magnitude and proper motion, it is essential that we should know approximately what percentage of the stars of such a group have twice, three times, &c., the mean parallax of

the group, and what percentage only one-half, one-third of that parallax, and so on. In principle, at least, this frequency-law may be obtained by means of the directly determined parallaxes. For the stars of which we have reliable determinations we can compare these true parallaxes with the *mean* parallax of stars having corresponding magnitude and proper motion, and this comparison will lead to a knowledge of the frequency-law required. It is true that, owing to the scarcity of material at present available, the determination of the frequency-law is not so strong as may be desirable, but further improvement is simply a question of time and the augmentation of parallax-determination.

Adopting provisionally the frequency-law found in this way by Kapteyn, we can localise all the stars in space down to about the ninth magnitude (*Publications Astron. Lab. Groningen*, No. 8, p. 23).

Take, for example, the stars of magnitude 5·5 to 6·5. There are about 4800 of these stars in the whole sky. According to Auwers-Bradley, about 9¼ per cent of these stars, or some 460 in all, have proper motions between 0·04" and 0·05." Now, according to Kapteyn's empiric formula, whose satisfactory agreement with the Yale results has just been shown, the mean parallax of such stars is almost exactly 0·01." Further, according to his frequency-law, 29 per cent of the stars have parallaxes between the *mean* value and double the mean value; 6 per cent have parallaxes between twice and three times the mean value; 1¼ per cent between three and four times the mean value. Therefore of our 460 stars 133 will have parallaxes between 0·01" and 0·02", twenty-eight between 0·02" and 0·03", seven between 0·03" and 0·04", and so on.

Localising in the same way the stars of the sixth magnitude having other proper motions, and then treating the stars of the first magnitude, second magnitude, third magnitude, and so on to the ninth magnitude in the same way, we finally locate all these stars in space (*Ibid.*, No. 11, Table II.).

It is true we have not localised the individual stars, but we know approximately and within certain limits of magnitude the number of stars at each distance from the Sun.

Thus the apparent brightness and the distance being known we have the means of determining the light-energy or absolute *luminosity* of the stars, *provided it can be assumed that light does not suffer any extinction in its passage through interstellar space.*

On this assumption Kapteyn was led to the following results, viz., that within a sphere the radius of which is 560 light-years (a distance which corresponds with that of the average star of the ninth magnitude) there will be found :—

1 star	giving from	100,000	to	10,000	Times the light of our Sun.
26 stars	,,	10,000	,,	1,000	
1,300 ,,	,,	1,000	,,	100	
22,000 ,,	,,	100	,,	10	
140,000 ,,	,,	10	,,	1	
430,000 ,,	,,	1	,,	0·1	
650,000 ,,	,,	0·1	,,	0·01	

(To be continued).

Dichloro-chromic Bromide and Dibromo-chromic Chloride.—Neils Bjerrum.—When green chromic bromide is dissolved in dilute hydrochloric acid and precipitated with hydrochloric acid gas, meanwhile cooling with cold water, a salt is obtained, which may be filtered off when the liquid is saturated with hydrochloric acid. Analysis shows that this salt has the formula $CrBr_2Cl.6H_2O$ or $[Cr(H_2O)_4Br_2]Cl.2H_2O$. The dichloro-chromic bromide is obtained by dissolving dichloro-chromic chloride in water and adding hydrobromic acid. It is a green deliquescent crystalline powder, with the formula $[Cr(H_2O)_4Cl_2]Br$. A tetrahydrate of dibromo-chromic bromide may be prepared from chromic acid and hydrobromic acid.—*Berichte*, xl., No. 19.

EXAMINATION OF RUBBER TYRES.

By CLAYTON BEADLE and HENRY P. STEVENS.

We have devoted a considerable amount of time and attention to the analysis and valuation of tyre rubbers, and think the results of our tests and observations will prove of general interest, as well as of practical utility. Of previous work, an interesting paper was published by the late C. O. Weber in the *Indiarubber Journal* dealing with the methods of analysis and significance of results obtained with bicycle tyres. A paper also appeared, by Schidrowitz and Kaye, in the *Journal of the Society of Chemical Industry*, Feb. 28th, 1907, giving the results of analyses obtained with a number of motor tyres; the analyses are given in detail. The results we shall here describe have been obtained with solid tyres, as the problems involved are, perhaps, simpler than with the outer cover of pneumatic tyres, where the tread is often composed of a different class of rubber to the remainder. We think, however, that most of what follows will also apply to outer covers, especially to that portion forming the tread.

The constituent of the tyre first calling for attention is the rubber itself. Although the quality of a tyre is by no means wholly dependent on the percentage of actual rubber substance or caoutchouc it contains, yet this percentage is of considerable importance in judging the value of a tyre. A satisfactory tyre cannot be made without a certain minimum percentage of rubber, although an experienced maker may succeed in producing an article of the same quality as his rival while using a smaller proportion of rubber. Any mixing, whatever the proportion of rubber, may be spoilt by errors in the manufacturing processes.

When interpreting the figure for the percentage of rubber found in the analysis of a tyre two other circumstances must be taken into consideration. The first of these is the kind of rubber used. Here we are working very much in the dark; there are data such as the percentage of resin from which some information may be gleaned, but it is difficult to draw trustworthy conclusions. The other point arises from the increasing use of recovered rubber in rubber mixings. Recovered rubber is of less value than new rubber, but analytical methods do not allow of a distinction being drawn except indirectly by the figure for vulcanisation coefficient. This latter represents the percentage of sulphur in actual chemical combination with the rubber or caoutchouc. As the methods employed in recovering waste rubber do not actually devulcanise, that is, remove combined sulphur, and as the recovered rubber when vulcanised probably combines with a further proportion of sulphur, it follows that tyre rubbers containing much recovered rubber have usually exceptionally high vulcanisation coefficients. Unfortunately, the determination of the latter involves three or four separate sulphur determinations, so that it is confined to careful and exhaustive analyses.

However, in spite of these limitations the figure for the percentage of rubber is of considerable value. It cannot be determined directly, but is obtained by difference after determining the acetone extract (chiefly resins and free sulphur), loss on boiling with alcoholic potash (rubber substitutes), and mineral matter. The latter is, of course, obtained by burning the rubber to ash.

The next figure to be considered is the percentage of matter extracted with acetone (acetone extract). This contains all free sulphur and resins. The free sulphur should not be too high, especially in the case of motor tyres which get very hot from friction. A high percentage of resin points to the use of inferior quality of rubber in the manufacture. Although the percentage of resin in a crude rubber is not proportional to the value of the rubber, nevertheless the better class of South American rubbers contain less resin in the washed and dried state than most African brands, and para contains less resin than any other variety. Indiarubber substitutes are undesirable in any class of tyre. The amount present may be judged by the loss

sustained on boiling the sample with alcoholic potash. The tensile strength is of great importance in judging the value of a tyre; as a general rule, the higher the tensile strength the better the tyre, provided that this result is attained with due regard to elasticity and distensibility. On the other hand, with certain classes of tyres, such as solid tyres, the distensibility should not be too great, otherwise the tyre is not sufficiently rigid. In the case of motor tyres which get very hot in use, the heat test should be applied. The samples are heated to a certain temperature for a definite period, and afterwards examined to see if, and to what extent, the rubber has deteriorated. The tensile strength may also be taken while the sample is hot; in this way the test is carried out under conditions which more closely resemble those to which the rubber is exposed in actual practice.

Finally, the tendency to sun cracking may be gauged by special chemical tests. This and others are described more fully at the end of this paper.

To demonstrate the aid afforded by the chemical and physical tests we have described, in forming an opinion of the value of a tyre and how it is likely to behave in use, we have chosen for illustration the results obtained in the examination of four samples, the relative merits of which we desired to ascertain.

Sample.	1.	2.	3.	4.
Resins, &c. (acetone extract), per cent.	9·0	8·6	7·2	7·4
Indiarubber substitutes (alcoholic potash extract), per cent	10·2	8·9	9·1	11·7
Mineral matter (ash), per cent	38·5	39·2	40·7	33·2
Indiarubber (caoutchouc) by difference, per cent	42·3	43·3	43·0	47·7
Total sulphur (calculated on caoutchouc), per cent ..	7·8	9·0	10·0	11·3
Free sulphur (calculated on caoutchouc), per cent ..	3·5	3·7	5·6	6·1
Combined sulphur (calculated on caoutchouc), per cent ..	4·3	5·3	4·4	5·2
Tensile strength, grms. . ..	3718	2509	3403	3217
Elongation at rupture, per cent)	55	38·5	52	45·5
Elongation under a strain of 1500 grms., per cent	23·5	24	24·5	26·5

In addition to the above figures it should be stated that the dry heat test did not bring out any striking differences between the four samples, although Samples 1 and 2 showed up as somewhat inferior to 3 and 4. The absorption of oxygen in the sun-cracking tests was practically the same in all four samples, and was not excessive.

We will now consider these results. To begin with, the figures obtained in the analysis of Sample 4 differ from Samples 1 to 3 in the small proportion of mineral matter and corresponding high percentage of caoutchouc. This at first sight seems to point to the surperiority of Sample 4 were it not that the vulcanisation coefficient (combined sulphur) is high, which points to the possibility that part of the caoutchouc is in reality recovered rubber. The extract with alcoholic potash is also higher than in the other samples, which is, of course, to its disadvantage. There is little to choose in this respect between Samples 2 and 3, while Sample 1 contains rather more. The acetone extracts of all four samples show about the same figure; Sample 1 is rather inferior in this respect. The percentage of free sulphur, provided that it is within certain limits, is not a matter of great importance in a solid tyre; this figure is highest in the case of Sample 4. The percentage of combined sulphur is, on the other hand, of great importance, the high figures in Samples 2 and 4 point to over-vulcanisation or the presence of substitutes, and mark these two samples as inferior to the others. These conclusions are borne out by the physical tests. The tensile strengths of Samples 2 and 4 are lower than the others; this applies especially to Sample 2, which is also wanting in distensibility, showing a smaller elongation at rupture than the other samples. The figures for tensile strength and elongation of Sample 4 are particularly instructive. Containing, as it apparently does, a larger percentage of caoutchouc and a smaller percentage of mineral matter, we should have expected it to show a higher tensile strength and elongation than Samples 1 and 3, which, for reasons referred to, is not necessarily the case. We have little hesitation in ranking Samples 2 and 4 as inferior to 1 and 3, and considering the very low tensile strength of Sample 2, we should think, on the whole, that it would be inferior to Sample 4. We now have to decide which of Samples 1 and 3 is the better. In tensile strength No. 1 has the advantage, but the acetone and alcoholic potash extracts are higher, which means that in this respect No. 1 is inferior. No. 1 did not behave so well as No. 3 in the heat test. The small elongation under a medium strain must be taken in favour of No. 1. Taking all matters into consideration we should give the preference to Sample 3. After the above analyses had been made and these conclusions drawn, the four samples were submitted to a rubber manufacturer, who, without a knowledge of our analytical figures, informed us, after an examination of the samples, the relative prices at which each could be produced. He stated that Sample 3 would be the most expensive to produce, Sample 1 coming next, while the samples of Samples 2 and 4 would be the cheapest to produce. It will therefore be seen that the conclusions drawn from our test were confirmed from a purely practical standpoint. We also learnt from an independent source that Sample 3 is one of the most satisfactory tyres on the market.

It would therefore appear that a thorough chemical and physical examination of a tyre will lead to a reliable estimation of its value.

In conclusion, we give a short description of the analytical methods.

As a result of our experience in analyses of tyre rubbers we have adopted the following methods for ordinary commercial purposes. The methods are based on the work of well-known authorities, as Henriques and Weber.

Portions are cut from the tyre and reduced to powder by passing through a mincing machine, and sufficient of the sample placed in a stoppered bottle for analysis. The mineral matter is determined by burning 1 grm. spread in an even layer on the bottom of a large porcelain crucible or small shallow dish; platinum crucibles cannot be used owing to the presence of zinc and other metals in the ash. Rubber is one of the most difficult substances to ash. It must be heated first with quite a small flame, and the rubber must not allowed to catch fire. The heating is continued, increasing the flame until the whole of the organic matter is burnt off. It should be allowed to cool in a desiccator, and weighed as soon as cold. In all cases it should be re-heated and weighed again.

The percentage of ash may be a little higher or lower than that of the mineral in the original mixing, as the mineral may contain some volatile constituents, *e.g.*, carbonic acid in the form of carbonate, and, on the other hand, some of the sulphur from the rubber may be retained by the metals as sulphides in the place of oxides, thus raising the weight of the ash. Nevertheless, the percentage of ash is a fairly accurate measure of the amount of mineral in the original mixing.

The specific gravity determination has lost much of its value as a means of detecting adulteration, owing to the use of rubber substitutes and recovered rubber. Further, it is obvious that the specific gravity of the added mineral will also produce its effect. Nevertheless, the figures for the specific gravity often bear a relation to those for ash. Take the following four samples from different sources which we recently had occasion to analyse for purposes of comparison:—

No. of sample.	Per cent ash.	Specific gravity.
1.	38·6	1·45
2.	40·9	1·51
3.	42·2	1·56
4.	42·4	1·59

We next proceed to a systematic examination to determine resin, free sulphur, and rubber substitutes. For this purpose 2 grms. of the finely powdered sample are thoroughly extracted for several hours in a Soxhlet with acetone. It is advisable to keep the extraction going for eight to ten hours. The acetone is distilled off, and the flask containing the resin and free sulphur dried in a water-oven and weighed. The contents are then exhausted four times with acetone, 2 cc. at a time, to dissolve out the resin, as suggested by Weber, and the sulphur remaining in the flask determined by drying down and weighing. A trace of sulphur dissolved by the acetone may be allowed for, but, according to Weber this only amounts to 6 mgrms. The sulphur subtracted from the total extract gives the resin. The extracted rubber is placed in a small weighing bottle, and dried in a current of coal-gas by taking out the stopper and inserting in its place a cork with inlet and outlet tubes; the coal-gas passing through is burnt underneath the water-oven in which the bottle is placed. The bottle is removed from time to time, the stopper inserted, and weighed when cold. The weight of the extracted rubber subtracted from that of the original rubber gives a rather higher figure for loss on extraction than that obtained by weighing the acetone extract. This is due to moisture in the original rubber.

The extracted rubber is introduced into a flask with inverted condenser, and boiled with weak alcoholic potash for four hours. It is then thrown on to a filter-paper and washed with hot water till no longer alkaline. The contents are transferred to the weighing-bottle, dried in a current of coal-gas as before, and weighed. The loss in weight may be taken as substitutes.

The residue will consist of rubber and mineral matter. It may be burnt to ash, and the rubber determined by difference.

We are now able to form a general opinion of the composition of the tyre. Of course it is possible to carry the analysis much further, chiefly with a view to determining the percentage of sulphur combined with the rubber or "vulcanisation coefficient." This figure is of value, but unfortunately its determination entails a good deal of analytical work.

Valuable as are the results of chemical analysis, there are certain physical tests which are of equal importance, in particular the determination of tensile strength and elongation at rupture. The most convenient method to adopt is to cut rings from sections of the tyre in thin sheets about 1 mm. thick. Discs are first cut, and the thickness of each disc is measured before puncturing. The ring is stretched between smooth iron hooks in a testing machine, and subjected to increasing tension until the ring ruptures. The tension required to rupture the ring and the elongation at the moment of rupture are noted.

The sun-cracking test is carried out by exposing thin sections of the tyres under examination to the action of a mixture of 20 grms. acetone and 60 cc. hydrogen peroxide solution (Weber). The test is a comparative one, so that the sections of tyres must be cut so as to expose the same area to the action of the mixed solutions. The pieces are weighed before immersion, and after twenty-four hours are removed, washed with a little acetone, dried, and weighed again. The increase in weight gives the amount of oxygen absorbed by the rubber, and may be taken as an indication of the tendency of the tyre to oxidise, which is the cause of "sun-cracking."

The "dry heat" test is carried out by exposing sections cut from the tyres to a temperature of 320° F. for four hours. For this purpose an ordinary hot-air oven provided with thermometer is required, and the temperature must be carefully regulated.

PRESENTATION OF ADDRESSES TO PROFESSOR LUNGE.

The students of the Zurich Polytechnic—and especially those of the Chemical Department, to whom the retirement of Prof. Lunge is so great a loss—did not allow his final lecture to pass by without offering him some tokens of their gratitude and affection. The Professor had expressed the wish that no elaborate ceremony should be arranged, but the informal gathering gave an impressive indication of the depth of the students' feelings. The vestibule and auditorium of the Chemical Department were decorated with laurel and other leaves, in preparation for the last lecture, and the whole building was closely packed with the students, colleagues, and friends of the Professor.

When Prof. Lunge entered the auditorium, greeted by the sounds of an Adagio played by the Students' Quartette, Prof. Treadwell rose and announced that he had been deputed by the teachers of the Institution to address a few words to him. He alluded to the length of Dr. Lunge's connection with the Polytechnic, and to the great value of the work he had done for it, to his unwearied efforts on behalf of the students, his phenomenal power of work and keen sense of duty, and to the esteem and gratitude which his colleagues felt for him. In conclusion, Prof. Treadwell expressed the hope that after a thorough rest for mind and body, he might feel sufficiently refreshed to take up again the life-work to which he had devoted all his strength and energy—the advancement of science—and that he might be spared for many years of activity. At the conclusion of his speech he read the text of an Address which the whole teaching staff of the Polytechnic presented to the retiring Professor.

Herr cand. chem. Walter Eglin then offered in heartfelt terms the thanks of the students, who honoured Prof. Lunge, not only as an inimitable teacher and a skilled experimenter, but also as a noble man whose example and counsel were invaluable to them when they embarked upon their varied careers. An Address from the students was then presented to Prof. Lunge, who rose to express his thanks. Almost overcome by emotion, he explained how impossible it was for him to put into words the deep feelings which had been aroused by this ceremony, and by the severance of his official connection with the Institution, upon the staff of which were some of his oldest and most valued friends. He said that ever since, acting on the advice of his physician, he had decided to vacate his post, he had hardly had a peaceful moment, for he could not conceive what it would mean to him to renounce an occupation which had hitherto absorbed all his time and energies. The farewell of his students had now, if possible, made his heart still heavier; the trouble they had taken to decorate the building, the closely-packed assembly in the hall, the kind words—far above his deserts—which Prof. Treadwell and Herr Eglin had spoken, all this recognition of his efforts he could only regard as implying that they took the will that he had to serve them for his imperfect deeds, and he felt that the memory of this leave-taking would be a consolation to him for the rest of his life, helping him through many dark hours.

Upon the conclusion of the speech, the whole audience rose and gave expression to their feelings in hearty applause, which Prof. Lunge repeatedly acknowledged. Thus ended the little ceremony, which in its simplicity and spontaneity testified admirably to the genuine warmth of the students' feelings and the affection of his colleagues.

Society of Arts.—The Council are prepared to offer, under the terms of the Stock Trust, a Gold Medal, or a Prize of £20, for the Decoration of Part of the Interior of a Building.

NOTICES OF BOOKS.

Les Nouveautés Chimiques pour 1907. ("Chemical Novelties for 1907.") By CAMILLE POULENC. Paris: J. B. Baillière et Fils. 1907.

THIS descriptive list of all the more important modifications and improvements of apparatus which have come into use during the year 1906, like its predecessors, will be a useful guide for equipping a physical or chemical laboratory with the most modern appliances. The author appears to have overlooked no important improvement in old, or invention of new apparatus, and has selected his material carefully and judiciously. Some allusion is made to the results of recent researches, and the section on chemical analysis is particularly full. Thus the analysis of milk by Bordas and Touplan's method is discussed at length, these chemists having found that the usual methods of estimating its constituents either leave something to be desired in the way of accuracy, or else are too slow to be employed when a great number of samples have to be examined. The method they propose has the advantage of allowing a series of six samples to be analysed fully in less than three hours, and the casein is determined directly and not by difference.

CORRESPONDENCE.

RELATION BETWEEN VALENCY AND ENERGY.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS (xcv., 301) Mr. Redgrove criticises an hypothesis of mine which appeared in the *Proc. Chem. Soc.*, xxiii., 134, as a preliminary note. I would therefore ask you to kindly insert the following reply:—

It is stated in the CHEMICAL NEWS, xcv., 193, that C is the heat of combustion of C in the hydrocarbons without the links, and H that of H with the C—H link. The latter is assumed to be different from the C.C link, which possesses a value L_1. It is stated that :C: in CH_4 is different from its value in C_2H_6 or in C_6H_{12}.

One of Mr. Redgrove's constants (·) is 2H $L_1 - 52{\cdot}7$, and it may also be shown that $C + 2L_1 = 105{\cdot}4$. If it be supposed that the amount added to the value of hydrogen is L, and also that $L = L_1$, the above constants may be stated as follows:—$H + \frac{L_1}{2} = H. = 26{\cdot}35$, $C + 4\frac{L_1}{2} = :C: = 105{\cdot}4$. These values are those of the isolated atoms on the above hypothesis.

It may, however, be shown by direct calculation that the numbers in question are those of the apparent atomic heats of combustion of H and C:—$2H = M.H.C.CH_4 - [CH_2] = 210{\cdot}8 - 158{\cdot}2 = 52{\cdot}6$, $H = 26{\cdot}3$; also $2H = M.H.C.\ C_2H_6 - 2[CH_2] = 52{\cdot}6$, $H = 26{\cdot}3$, $C = 158{\cdot}2 - 52{\cdot}6 = 105{\cdot}6 = 4 \times 26{\cdot}4$.

These results clearly show that $L = L_1$ whatever these may be, and, further, that they are both equal to zero, for it is evident, from the additive relations, that the numbers 26·3 and 105·6 represent either the values of the isolated atoms or that the heats concerned in the breaking and making of an equal number of links in such an equation as $C{\equiv}H_4 + 2O = O = C{\leq}^{O}_{O} + 2H{>}O$ exactly compensate one another.

The values L and L_1 have thus no significance when used in the above connection, and may therefore be neglected.

If the links be taken into account (on the latter assumption), it follows that :C: : H. = X : Y, numbers $>$ 105·6 and $>$ 26·3 respectively; that is, $>$ the apparent atomic heats of combustion of C and H.

If the unknown values :C: and H., however, be considered, it follows from the fact that $:C: = C + 4\frac{L_1}{2} = X$ and $H. = H + \frac{L_1}{2} = Y$ that the values of the isolated atoms are still in the ratio of 4 : 1, which is similar to the ratio between their valency numbers.

Mr. Redgrove further states that my hypothesis is wrong because two out of the four carbon links show considerably large values. It will be found that the formulæ applying to the olefins and acetylenes are respectively (*a*) M.H.C. $C_nH_{2n}| = | = 6n\,c + |$, and (*b*) M.H.C. $C_nH_{2n-2}|{\equiv}| = 6n\,c - 2c + |{\equiv}|$; $|=|$ and $|{\equiv}|$ representing additional heat values, which are constant. This is evident if we study a column (Column 11, Table I.) of so-called errors:—Olefins $|=|$, $-17{\cdot}2$, $18{\cdot}8$, $18{\cdot}9$; diolefins $|=|_2$, $-37{\cdot}3 = 2 \times 18{\cdot}65$; acetylenes $|{\equiv}|$, $-46{\cdot}2$, $46{\cdot}7$; diacetylenes $|{\equiv}|_2$, $-93{\cdot}9 = 2 \times -46{\cdot}95$. It is thus inadmissible to apply the relation $c = \frac{\text{M.H.C.}}{\text{Valency number}}$ to the above compounds, as Mr. Redgrove has done.

The additional heat values that have just been considered do not invalidate the valency rule, but constitute a peculiarity which calls for special explanation. Although characteristic of the $|=|$ and $|{\equiv}|$ links, they are by no means limited to these, for trimethylene, C_3H_6, which is incapable of reacting additively without a rupture of the ring, also possesses an additional heat value. The extra free energy of which the above is a sign may be supposed to give rise to intra-molecular tension, and also explains the extraordinary reactivity and instability of the compounds. They may in some cases be susceptible to spontaneous explosion—a fact which does not seem capable of explanation on any other hypothesis.

Finally, Mr. Redgrove obtains a mean value of $c = 26{\cdot}25$. I cannot obtain this number from the values given in Column 4, Table I.—I am, &c.,

GERVAISE LE BAS.

The Municipal School of Technology, Manchester.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 10, 1907.

Decomposition of Gaseous Hydrocarbons by Heating with Finely-divided Aluminium.—M. Kusnetzow.—When a dried hydrocarbon is led over a tube containing aluminium which is heated till it just begins to melt, it is found that the gaseous product of the reaction is almost pure hydrogen, while all the carbon is deposited in the tube. The author's experiments extended to methane, ethane, ethylene, and acetylene, which were obtained by the reduction of their haloid compounds. Thus aluminium decomposes the hydrocarbons into their elements, the hydrogen escaping in the free state, while the carbon is partly deposited mechanically upon the surface of the aluminium (and may be burnt to carbon dioxide by ignition in air), and partly forms a carbide which, when warmed gently with water, gives impure methane, among other hydrocarbons.

Action of Sodium Arsenite upon Sodium Ethyl Thiosulphate.—A. Gutmann.—When sodium arsenite acts upon sodium thiosulphate the latter is converted into sulphite and the arsenite into sodium monosulphoxyarsenate, $S_2O_3Na_2 + AsO_3Na_3 = Na_2SO_3 + AsSO_3Na_3$. It was therefore to be expected that if sodium ethyl thiosul-

phate was substituted for the thiosulphate, sodium ethyl sulphonate or sulphite, $SO_2(ONa)C_2H_5$ or $SO_2(Na)OC_2H_5$, would be obtained, according to the equation $S_2O_3NaC_2H_5 + AsO_3Na_3 = SO_3NaC_2H_5 + AsSO_3Na_3$. The author has, however, found that this reaction does not occur, for a strong smell of thioalkyl compound is produced. There are three possible explanations. The most obvious explanation would be the saponification of the sodium ethyl thiosulphate in presence of caustic soda, $S_2O_3NaC_2H_5 + NaOH = SO_4Na_2 + C_2H_5.SH$ or $H_2S_2O_3 = SO_3 + H_2S$, but no trace of sulphate was formed although mercaptan was present. Thus, this explanation could not be correct. The two remaining possibilities are represented by the equations—

$$2S_2O_3NaC_2H_5 + 2NaOH + AsO_3Na_3 = 2SO_3Na_2 + C_2H_5S_2C_2H_5 + AsO_4Na_3 + H_2O$$

or—

$$2S_2O_3H_2 = 2SO_2 + S_2H_2 + O + OH_2,$$

and—

$$2S_2O_3NaC_2H_5 + 2NaOH + 2AsO_3Na_3 = 2SO_3Na_2 + 2C_2H_5SH + 2AsO_4Na_3$$

or—

$$2S_2O_3H_2 = 2SO_2 + 2SH_2 + 2O.$$

When the reaction was investigated quantitatively it was found that the last equation represents the transformation which occurs, and the final products are sulphite, ethyl mercaptan, and tertiary sodium arsenate. It is very noteworthy that arsenate should be formed from a sulphite. The decomposition, $S_2O_3H_2 = SO_2 + SH_2 + O$, explains why, when sodium stannite acts upon sodium thiosulphate, no sulphate but black stannous sulphide is formed. The equation representing the reaction which occurs is—

$$2Sn(ONa)_2 + S_2O_3Na_2 + H_2O = SnS + SO_3Na_2 + SnO_3Na_2 + 2NaOH.$$

Thus, thiosulphate undergoes the three reactions :— $S_2O_3H_2 = SO_2 + S + H_2O$, $S_2O_3H_2 = SO_3 + H_2S$, $S_2O_3H_2 = SO_2 + O + SH_2$.

Action of Ozone on Metallic Silver and Mercury.—W. Manchot and W. Kampschule.—The blackening of silver by means of ozone is most readily effected when the metal is first heated to incipient red heat. By a series of experiments in which the temperature of a silver tube was accurately fixed by boiling a pure liquid of known boiling-point in it, the effects at different temperatures were studied. At 100° a milk-white deposit is formed ; at 154° a dark blue or steel-blue film appears ; and between 220° and 240° the action is most marked. Above this temperature it becomes feebler, and at 450° no change is perceptible. These experiments were carried out with carefully dried ozone. With damp ozone the same results were obtained, but all these statements hold good only if the surface of the silver is quite clean. The authors find that the blackening of silver in the cold even by very dilute ozone is due to the presence on its surface of very minute quantities of some substance such as oxide of silver, cobalt, nickel, &c., which acts as a catalytic oxygen carrier. Even when the metal is heated to redness traces of oxide remain on its surface. Mercury behaves in the same way as silver towards ozone. The effect first increases, and then decreases, and finally disappears, though the temperature intervals in which the changes take place are somewhat lower.

Products of Dehydration of Dichloro-chromic Chloride.—Neils Bjerrum.—When green chromic chloride, $CrCl_3.6H_2O$, is allowed to stand over phosphorus pentoxide in a vacuum of 1 mm. for twenty days, it yields a red modification, probably with one and a-half molecules of water, or possibly its formula is $CrCl_3.2H_2O$, and it slowly gives up water. This new modification is very deliquescent, giving a greenish yellow solution with water, which turns blue-violet on standing. The electric conductivity of the salt at 25° is smaller than that of a solution of the green chloride, but very rapidly rises. The solution therefore probably contains less chlorine in the form of chlorine ions than a solution of dichloro-chromic chloride, and the splitting off of water from the tetrahydrate is not accompanied by a deep-seated change in the constitution of the salt. When dehydrated at a higher temperature in a current of chlorine, five and a-half molecules of water escape, and a red substance is left. At 0° this substance is rapidly and apparently completely dissolved, giving a red solution, but after a short time a red precipitate separates, which again dissolves after standing for a day. Probably the chromic chloride is converted by heating into the colloidal form, which first dissolves, but is precipitated if the solution possesses a certain amount of salting out electrolyte formed owing to the change of the chloride.

Heat of Formation of Phosphorus Nitride, P_3N_5.—Alfred Stock and Franz Wrede.—The authors employed a Krœker's bomb with a platinum resistance thermometer to determine the heat of combustion of phosphorus nitride. The bomb was lined with enamel, and a porcelain crucible was used, while the platinum lining of the lid was protected by mica. When the nitride burns phosphorus pentoxide is formed, as well as free nitrogen, and fills the whole bulb with a white mist, taking up any water present. This reaction takes some time and much heat is developed, so that it is necessary to determine accurately the water present, or it is better to perform the combustion in perfectly dry oxygen. The nitrogen which is oxidised cannot be estimated as nitric acid, but the resulting nitric oxide has to be determined by another method. The authors condensed the gaseous contents of the bomb in liquid air, and allowed the oxygen to boil away. The nitric oxide remained behind quantitatively, and was vaporised by heating and receiving it into titrated caustic potash. It was thus found that for 1 grm.-mol. of P_3N_5 (163 grms.) the heat of combustion at constant temperature is 473·2 cals. and at constant pressure 474·7 cals. These figures relate to the decomposition of the nitride to P_2O_5 and N. To calculate the heat of formation of P_3N_5 it is necessary to determine the difference between the heats of combustion of free phosphorus and P_3N_5. The results are as follows :—

For Colourless Phosphorus—

Heat of combustion of { P to P_2O_5 = $3 \times 370{\cdot}8 = 1112{\cdot}4$ cals.
P_3N_5 = $-2 \times 474{\cdot}7 = 949{\cdot}4$,,

$2P_3N_5 = 163{\cdot}0$,,

Therefore, heat of formation of $P_3N_5 = +81{\cdot}5$ cals.

For Red Phosphorus—

Heat of combustion of { P to P_2O_5 = $3 \times 363{\cdot}4 = 1090{\cdot}2$ cals.
P_3N_5 = $-2 \times 474{\cdot}7 = 949{\cdot}4$,,

$2P_3N_5 = 140{\cdot}8$,,

Therefore, heat of formation of $P_3N_5 = 70{\cdot}4$ cals.

Preparation and Properties of Fluorides of Hexavalent Molybdenum.—Otto Ruff and Fritz Eisner.—Molybdenum hexafluoride may be prepared by allowing molybdenum pentachloride and anhydrous hydrofluoric acid to act upon one another at about 30—40°, or by the addition of bromine and antimony pentafluoride to the pentachloride. To obtain it in the pure state it is best to allow pure fluorine to act on metallic molybdenum. It is a soft crystalline mass, melting at 17° to a colourless liquid which boils at 35°. Its colourless vapour gives a blue-white mist in air. It is very sensitive to moisture and decomposes with a little water giving blue molybdenum oxides. With much water it gives a colourless solution. It does not decolorise permanganate, but is easily and completely absorbed by ammonia and alkalis. With alkali fluorides it forms double compounds. The oxytetrafluoride, $MoOF_4$, results when molybdenum oxytetrachloride is treated with anhydrous hydrofluoric acid. It is a white very hygroscopic solid at ordinary temperatures, becoming blue, and deliquescing in the air. It melts at 97—98° and boils at about 180°, and its density at the temperature of the room is 3·001. It gives a colourless solution with water and alcohol, and light-green or yellow

solutions with ether and chloroform; when the aqueous solution is evaporated molybdenum trioxide is deposited, while a white mass is left when the other solutions are evaporated. It is insoluble in toluene, almost insoluble in benzene and carbon disulphide; it gives a colourless solution with concentrated sulphuric acid, hydrofluoric acid being evolved. With phosphorus trichloride and oxychloride, arsenic trichloride, and sulphur monochloride it gives brown solutions. Molybdenum dioxydifluoride is formed when molybdenum trioxide is ignited with fluorides, *e.g.*, lead fluoride or kryolite, or when anhydrous hydrofluoric acid reacts with molybdenum dioxydichloride. It is a white hygroscopic solid like the oxytetrafluoride, turning green in air and deliquescing. It sublimes at 265—270°, and its density is 3·494. It gives a blue solution with a little water, and a colourless solution with much water. It is almost insoluble in ether, chloroform, and carbon tetrachloride, and completely insoluble in toluene. It dissolves to a colourless solution in arsenic trichloride, silicon tetrachloride, and sulphuryl chloride, and gives a blue solution with phosphorus trichloride. All these solutions on warming evolve gases. The reactions of the dioxydifluoride and oxytetrafluoride resemble those of the hexafluoride, but are less energetic. The comparison of the physical properties of the new fluorides with those of the corresponding compounds of tungsten illustrate the close connection between these two elements.

Electrolytic Dissociation of Fused Salts.—K. Arndt.—The calculation of the degree of dissociation of a dissolved electrolyte is performed according to Arrhenius's theory by comparing the conductivity of the solution with the limiting value to which its equivalent conductivity approaches as the dilution increases. This method could not be applied to fused salts because no solvent was known which did not conduct the electric current. The author has discovered that boric acid anhydride may be employed as such a solvent, for its conductivity for the purest Kahlbaum's preparation is only $K = 0{\cdot}000021$ at 900°, *i.e.*, it conducts as badly as distilled water. He used sodium metaphosphate as dissolved electrolyte, and measured the viscosity and conductivity at 900° with different percentages of the electrolyte in the melt. He found that the product conductivity × viscosity is constant, and thus the conductitity is proportional to the viscosity. Calculated for the same viscosity the equivalent conductivity is independent of the concentration. This surprising result is most simply explained by assuming that the fused sodium metaphosphate is completely dissociated. The same may hold good for potassium and sodium chlorides and other salts, and the assumption is supported by the fact that with all these salts the increase of conductivity with the temperature is represented by a straight line, which points to a simple constitution of the melts. The salts of divalent metals, *e.g.*, calcium chloride, give a conductivity curve, which first rises rapidly and then more gradually with the temperature, and finally approximates to a straight line. Hence it may be supposed that the dissociation is not complete at the melting-point, and that the salt is not completely split up till the temperature is further raised. This conclusion that fused monovalent salts are completely dissociated is confirmed by some work of Lorenz, which has not yet been published.

Ammonium Amalgam.—George McPhail Smith.—The author's experiments have shown that Le Blanc's conclusion that ammonium amalgam is a compound of mercury with the metallic radicle NH_4 is the correct view of its constitution, and that the assumptions of Moissan that it is a compound of ammonia and mercury hydride, and of Rich and Travers that it is free ammonium dissolved in mercury, are both untenable. Moissan based his view upon the fact that sodium amalgam containing sodium hydride reacts with aqueous ammonia with increase of volume, while sodium amalgam alone gives hydrogen at constant volume with the same liquid. The author repeated Moissan's experiments with some modifications, and found that although sodium amalgam does not increase in volume with aqueous ammonia, other amalgams do, and sodium amalgam itself swells up with ammonium salt solutions. Also at a lower temperature the NH_4· of the ammonium hydroxide present in the solution is capable of expelling sodium from its amalgam. Moreover, it has been found that in the form of their amalgams the alkali and alkaline earth metals are mutually replaceable, and since ammonium amalgam also possesses this property it must be regarded as a true analogue of potassium amalgam. There is no ground for Rich and Travers's assumption that ammonium amalgam is a simple solution of free ammonia in metallic mercury, and their experiments only show that the general formula of the amalgam is NH_4Hg_m. Cryoscopic measurements cannot determine m, and there is no reason for thinking that it is equal to o. Indeed, Moissan and Ruff's failure to isolate free ammonium at very low temperatures argues against this assumption. The author's experiments all go to show that ammonium amalgam is a compound of the formula $MeHg_m$, dissolved in free mercury. This compound, NH_4Hg_m, is very unstable; at 0° it decomposes slowly, and more quickly at room temperature into hydrogen, ammonia, and mercury. The gases are retained by the mass, and cause the characteristic swelling up, which, however, is not a property of the original compound, but is only an incidental phenomenon of its decomposition.

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INAUGURAL ADDRESS OF THE PRESIDENT,

Sir David Gill, K.C.B., LL.D., D.Sc., F.R.S., Hon. F.R.S.E., &c.

(Concluded from p. 55).

The Density of Stellar Distribution at Different Distances from our Sun.

Consider, lastly, the distribution of stellar density, that is, the number of stars contained in the unit of volume.

We cannot determine *absolute* star-density, because, for example, some of the stars which we know from their measured parallaxes to be comparatively near to us are in themselves so little luminous that if removed to even a few light-years greater distance they would appear fainter than the ninth magnitude, and so fall below the magnitude at which our data at present stop.

But if we assume that intrinsically faint and bright stars are distributed in the same proportion in space, it will be evident that the comparative richness of stars in any part of the system will be the same as the comparative richness of the same part of the system in stars of a particular luminosity. Therefore, as we have already found the arrangement in space of the stars of different degrees of luminosity, and consequently their number at different distances from the Sun, we must also be able to determine their relative density for these different distances.

Kapteyn finds in this way that, starting from the Sun, the star-density (*i.e.*, the number of stars per unit volume of space) is pretty constant till we reach a distance of some 200 light-years. Thence the density gradually diminishes till, at about 2500 light-years, it is only about *one-fifth* of the density in the neighbourhood of the Sun (*Publications Astron. Lab. Groningen*, No. 11). This conclusion must, however, be regarded as uncertain until we have by independent means been enabled to estimate the absorption of light in its course through interstellar space, and obtained proof that the ratio of intrinsically faint to bright stars is constant throughout the universe.

Thus far Kapteyn's researches deal with the stellar universe as a whole; the results, therefore, represent only the *mean* conditions of the system. The further development of our knowledge demands a like study applied to the several portions of the universe separately. This will require much more extensive material than we at present possess.

As a first further approximation the investigation will have to be applied separately to the Milky Way and the parts of the sky of higher galactic latitude. The velocity and direction of the Sun's motion in space may certainly be treated as constants for many centuries to come, and these constants may be separately determined from groups of stars of various regions, various magnitudes, various proper motions, and various spectral types. If these constants as thus separately determined are different, the differences which are not attributable to errors of observation must be due to a common velocity or direction of motion of the group or class of star to which the Sun's velocity or direction is referred. Thus, for example, the Sun's velocity as determined by spectroscopic observations of motion in the line of sight, appears to be sensibly smaller than that derived from fainter stars. The explanation appears to be that certain of the brighter stars form part of a cluster or group of which the Sun is a member, and these stars tend to some extent to travel together. For these researches the existing material, especially that of the determination of velocities in the line of sight, is far too scanty.

Kapteyn has found that stars whose proper motions exceed 0·05″ are not more numerous in the Milky Way than in other parts of the sky (*Verl. Kn. Akad. Amsterdam*, January, 1893); in other words, if only the stars having proper motions of 0·05″ or upwards were mapped there would be no aggregation of stars showing the existence of a Milky Way.

The proper motions of stars of the second spectral type are, as a rule, considerably larger than those of the first type; but Kapteyn comes to the conclusion that this difference does not mean a real difference of velocity, but only that the second-type stars have a smaller luminosity, the mean difference between the two types amounting to 2½ magnitudes (*Verl. Kn. Akad. Amsterdam*, April, 1892).

The Future Course of Research.

In the last Address delivered from this Chair on an astronomical subject, Sir William Huggins, in 1891, dealt so fully with the chemistry of the stars that it seemed fitting on the present occasion to consider more especially the problem of their motion and distribution in space, as it is in this direction that the most striking advances in our knowledge have recently been made. It is true that since 1891 great advances have also been made in our detailed knowledge of the chemistry of the Sun and Stars. The methods of astro-spectrography have been greatly improved, the precision of the determination of motion in the line of sight greatly enhanced, and many discoveries made of those close double stars, ordinarily termed spectroscopic doubles, the study of which seems destined to throw illustrative light upon the probable history of the development of systems from the original nebular condition to that of more permanent systems.

But the limitations of available time prevent me from entering more fully into this tempting field, more especially as it seems desirable, in the light of what has been said, to indicate the directions in which some of the astronomical work of the future may be most properly systematised. There are two aspects from which this question may be viewed. The first is the more or less immediate extension of knowledge or discovery; the second the fulfilment of our duty, as astronomers, to future generations. These two aspects should never be entirely separated. The first, as it opens out new vistas of research and improved methods of work, must often serve as a guide to the objects of the second. But the second is to the astronomer the supreme duty, viz., to secure for future generations those data the value of which grows by time.

As the result of the Congress of Astronomers held at Paris in 1887 some sixteen of the principal observatories in the world are engaged, as is well known, in the laborious task, not only of photographing the heavens, but of measuring these photographs and publishing the *relative* positions of the stars on the plates down to the eleventh magnitude. A century hence this great work will have to be repeated, and then, if we of the present day have done our duty thoroughly, our successors will have the data for an infinitely more complete and thorough discussion of the motions of the sidereal system than any that can be attempted to-day. But there is still needed the accurate meridian observation of some eight or ten stars on each photographic plate, so as to permit the conversion of the *relative* star-places on the plate into *absolute* star-places in the heavens. It is true that some of the astronomers have already made these observations for the reference stars of the zones which they have undertaken. But this seems to be hardly enough. In order to co-ordinate these zones, as well as to give an accuracy to the *absolute* positions of the reference stars corresponding with that of the *relative*

positions, it is desirable that this should be done for *all* the reference stars in the sky by several observatories. The observations of well-distributed stars by Kustner at Bonn present an admirable instance of the manner in which the work should be done. Several observatories in each hemisphere should devote themselves to this work, employing the same or other equally efficient means for the elimination of sources of systematic error depending on magnitude, &c., and it is of far more importance that we should have, say, two or three observations of each star at three different observatories than two or three times as many observations of each star made at a single observatory.

The southern cannot boast of a richness of instrumental and personal equipment comparable with that of the northern hemisphere, and consequently one welcomes with enthusiasm the proposal on the part of the Carnegie Institute to establish a meridian observatory in a suitable situation in the southern hemisphere. Such an observatory, energetically worked, with due attention to all necessary precautions for the exclusion of systematic errors would conduce more than anything else to remedy in some degree that want of balance of astronomical effort in the two hemispheres to which allusion has already been made. But in designing the programme of the work it should be borne in mind that the proper duty of the meridian instrument in the present day is no longer to determine the positions of all stars down to a given order of magnitude, but to determine the positions of stars which are geometrically best situated, and of the most suitable magnitude for measurement on photographic plates, and to connect these with the fundamental stars. For this purpose the working list of such an observatory should include only the fundamental stars and the stars which have been used as reference stars for the photographic plates.

Such a task undertaken by the Carnegie Observatory, by the Cape, and if possible by another observatory in the southern hemisphere, and by three observatories in the northern, would be regarded by astronomers of the future as the most valuable contribution that could be made to astronomy of the present day. Taken in conjunction with the astrographic survey of the heavens now so far advanced, it is an opportunity that if lost can never be made good; a work that would grow in value year by year as time rolls on, and one that would ever be remembered with gratitude by the astronomers of the future.

But for the solution of the riddle of the universe much more is required. Besides the proper motions, which would be derived from the data just described, we need for an ideal solution to know the velocity in the line of sight, the parallax, the magnitude, and the spectrum-type of every star.

The broad distinction between these latter data and the determination of proper motion is this, that whereas the observations for proper motion increase in value as the square of their age, those for velocity in the line of sight, parallax, magnitude, and type of spectrum may, for the broader purposes of cosmical research, be made at any time without loss of value. We should therefore be most careful not to sacrifice the interests of the future by immediate neglect of the former for the latter lines of research. The point is that those observatories which undertake this meridian work should set about it with the least possible delay, and prosecute the programme to the end with all possible zeal. Three observatories in each hemisphere should be sufficient; the quality of the work should be of the best, and quality should not be sacrificed for speed of work.

But the sole prosecution of routine labour, however high the ultimate object, would hardly be a healthy condition for the astronomy of the immediate future. The sense of progress is essential to healthy growth, the desire to know must in some measure be gratified. We have to test the work that we have done in order to be sure that we are working on the right lines, and new facts, new discoveries, are the best incentives to work.

For these reasons Kapteyn, in consultation with his colleagues in different parts of the world, has proposed a scheme of research which is designed to afford within a comparatively limited time a great augmentation of our knowledge. The principle on which his programme is based is that adequate data as to the proper motions, parallaxes, magnitudes, and the type of spectrum of stars situated in limited but symmetrically distributed areas of the sky, will suffice to determine many of the broader facts of the constitution of the universe. His proposals and methods are known to astronomers, and need not therefore be here repeated. In all respects save one these proposals are practical and adequate, and the required co-operation may be said to be already secured—the exception is that of the determination of motion in the line of sight.

All present experience goes to show that there is no known satisfactory method of determining radial velocity of stars by wholesale methods, but that such velocities must be determined star by star. For the fainter stars huge telescopes and spectroscopes of comparatively low dispersion must be employed. On this account there is great need in both hemispheres of a huge reflecting telescope—six to eight feet in aperature—devoted almost exclusively to this research. Such a telescope is already in preparation at Mount Wilson, in America, for use in the northern hemisphere. Let us hope that Professor Pickering's appeal for a large reflector to be mounted in the southern hemisphere will meet with an adequate response, and that it will be devoted there to this all-important work.

Conclusion.

The ancient philosophers were confident in the adequacy of their intellectual powers alone to determine the laws of human thought, and regulate the actions of their fellow men, and they did not hesitate to employ the same unsupported means for the solution of the riddle of the universe. Every school of philosophy was agreed that some object which they could see was a fixed centre of the universe, and the battle was fought as to what that centre was. The absence of facts, their entire ignorance of methods of exact measurement, did not daunt them, and the question furnished them a subject of dispute and fruitless occupation for twenty-five centuries.

But astronomers now recognise that Bradley's meridian observations at Greenwich, made only 150 years ago, have contributed more to the advancement of sidereal astronomy than all the speculations of preceding centuries. They have learned the lesson that human knowledge in the slowly developing phenomena of sidereal astronomy must be content to progress by the accumulating labours of successive generations of men; that progress will be measured for generations yet to come more by the amount of honest, well-directed, and systematically discussed observation than by the most brilliant speculation; and that, in observation, concentrated systematic effort on a special thoughtfully selected problem will be of more avail than the most brilliant but disconnected work.

By these means we shall learn more and more of the wonders that surround us, and recognise our limitations when measurement and facts fail us.

Huggins's spectroscope has shown that many nebulæ are not stars at all; that many well-condensed nebulæ, as well as vast patches of nebulous light in the sky, are but inchoate masses of luminous gas. Evidence upon evidence has accumulated to show that such nebulæ consist of the matter out of which stars (*i.e.*, suns) have been and are being evolved. The different types of star spectra form such a complete and gradual sequence (from simple spectra resembling those of nebulæ onwards through types of gradually increasing complexity) as to suggest that we have before us, written in the cryptograms of these spectra, the complete story of the evolution of suns from the inchoate nebula onwards to the most active sun (like our own), and then downward to the almost heatless and invisible ball. The period during which human life has existed on our globe is probably too short—even if our first parents had begun the work—to afford observational proof of such a

cycle of change in any particular star; but the fact of such evolution, with the evidence before us, can hardly be doubted. I most fully believe that, when the modifications of terrestrial spectra under sufficiently varied conditions of temperature, pressure, and environment have been further studied, this conclusion will be greatly strengthened. But in this study we must have regard also to the spectra of the stars themselves. The stars are the crucibles of the Creator. There we see matter under conditions of temperature and pressure and environment, the variety of which we cannot hope to emulate in our laboratories, and on a scale of magnitude beside which the proportion of our greatest experiment is less than that of the drop to the ocean. The spectroscopic astronomer has to thank the physicist and the chemist for the foundation of his science, but the time is coming—we almost see it now—when the astronomer will repay the depth by wide-reaching contributions to the very fundamenta of chemical science.

By patient, long-continued labour in the minute sifting of numerical results, the grand discovery has been made that a great part of space, so far as we have visible knowledge of it, is occupied by two majestic streams of stars travelling in opposite directions. Accurate and minute measurement has given us some certain knowledge as to the distances of the stars within a certain limited portion of space, and in the cryptograms of their spectra has been deciphered the amazing truth that the stars of both streams are alike in design, alike in chemical constitution, and alike in process of development.

But whence have come the two vast streams of matter out of which have been evolved these stars that now move through space in such majestic procession?

The hundreds of millions of stars that comprise these streams, are they the sole ponderable occupants of space? However vast may be the system to which they belong, that system itself is but a speck in illimitable space; may it not be but one of millions of such systems that pervade the infinite?

We do not know.

"Canst thou by searching find out God? Canst thou find out the Almighty unto perfection?"

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

LEICESTER, 1907.

By Professor A. SMITHELLS, B.Sc., F.R.S., President of the Section.

THE year which has elapsed since the meeting of our Section at York has been eventful in the most melancholy of ways; the losses sustained by our science have been unparalleled. The passing bell seems to have tolled almost without intermission as one after another of our masters have been taken from us: in Russia, Mendeleeff, Menschutkin, and Beilstein; in France, Berthelot and Moissan; in Holland, Bakhuis-Roozeboom. Whilst in some of these cases we may find consolation in contemplating a length of life and sustained activity beyond what we might have dared to expect, in others our regret is increased by the sense of untimeliness and of vanished hopes. I am tempted to speak of the work of such mighty men as Berthelot and Mendeleeff, to dwell upon the discoveries by which they transformed the whole fabric of chemical science; but this is not the occasion on which to offer an estimate of the labours of those who have passed away. I can only say that in the bond of brotherhood which the pursuit of science establishes among the different nations of the earth we who are Englishmen feel and deplore these losses as our own.

I must not omit to allude also, as I do with deep regret, to the death in our own country of two such ardent and fruitful workers as Cornelius O'Sullivan and Robert Warington.

These words were already in print when again we were called to mourn the loss of one of our greatest men, one who but a year ago was the subject of our special rejoicings, and whose vigour of body and youthfulness of spirit seemed to promise the long continuance of a noble and an extraordinarily fruitful life. We can at least feel thankful that William Henry Perkin lived long enough to learn in what honour and esteem his name was held, not only among his countrymen, but by all the chemists of the world, and by the leaders of those great industries of which he was justly acclaimed the founder. For more than a generation Sir William Perkin had been one of the most familiar figures at the meetings of this Section, and greatly shall we miss his gentle presence, his wise counsel, and his valued contributions.

I can, perhaps, best occupy your time to-day by attempting to give some account of the present state of the scientific subject to which I have paid most attention. The topic of flame, after a long period of repose, has aroused much interest during late years, and I think we may say that some considerable progress has been made in its elucidation, although in this, as in all other subjects of scientific inquiry, the more closely we scrutinise it the more impressed must we be with what still remains unknown.

One of the first questions that meet us in the study of flame is that of the temperature at which in any given case the phenomenon becomes evident. Here, I think, a great clarification of view has taken place. The old idea that there existed a fixed temperature at which inflammation suddenly took place cannot now be maintained, and the term "ignition temperature" has acquired a different meaning. It is now known that in a very great number of cases a mixture of two flame forming gases, when gradually raised in temperature, will develop luminosity quite gradually, *pari passu*, with the chemical combination that is being induced. This phenomenon is, of course, known universally in connection with phosphorus, but it is not so widely known in connection with other combustible substances. There are some simple facts that seem as if they never could gain admission to text-books, and I do not think I have known more than a single chemical book that is not likely to leave a student under the impression that the phosphorescence of phosphorus is an almost unique phenomenon. I do not know how many times the independent discovery has been made that sulphur, arsenic, carbon disulphide, alcohol, ether, paraffin, and a whole host of other compounds, inorganic and organic, will phosphoresce as truly as phosphorus itself; that, in fact, phosphorescent combustion is the normal phenomenon antecedent to what we ordinarily call flame.

This is, after all, only in harmony with the general truth that chemical combination between two gases does not set in suddenly, but comes into evidence quite gradually as the temperature is raised from a point at which the action, if it occurs at all, is so slow as to be negligible. The increase in the rate of combination is, of course, very rapid as compared with the increase of temperature, a difference of about 10° C. serving to double it. The interval between the beginning of phosphorescence and the production of vigorous flames may therefore be very short. In the case of phosphorus this interval, being from 7° to 60° C., includes ordinary atmospheric temperatures; hence the phosphorescence of phosphorus is a phenomenon that could not well be overlooked. If the prevailing terrestrial temperature were below 7° C., at which, under normal air-pressure, the phosphorescence of phosphorus ceases, it is possible that this element might never have acquired its peculiar reputation; it would not have shown in the dark, and in lighting it with a taper the phosphorescent interval would have been passed over as quickly as is ordinarily the case in the ignition of sulphur, paraffin, and other common combustibles. To make phosphorescence apparent in these last cases it is necessary to take special care to heat up a mixture of the combustible gas and air gently, and to maintain it at a temperature approaching,

but not quite reaching, that of ignition. There is no simpler way than that used by Sir William Perkin, who brought the combustible substance near to, or in contact with, a massive metal ball previously heated to the suitable temperature.

The change from phosphorescence to ordinary flame is not sudden, but the appearance of ordinary flame is the end point of a continuous, though rapid, development. This end point is the temperature of ignition. What, then, determines the temperature of ignition? The answer to this question has been given with characteristic conciseness by van 't Hoff as "the temperature at which the initial loss of heat due to conduction, &c., is equal to the heat evolved in the same time by the chemical reaction."

We may obtain a clear idea of the meaning of temperature of ignition by supposing a combustible mixture of gases such as that of air and the vapour of carbon disulphide to issue through an orifice into an indifferent atmosphere. If we surround the orifice by a ring of platinum wire, which is gradually heated up by a current of electricity, a flame will gradually make its appearance. If, as soon as this is observed, the heating of the wire by the current be discontinued, the flame will disappear; it is, in fact, not self-supporting, but depends on the accessory supply of heat through the electrically heated wire. If now we raise the ring to a higher temperature we shall get a brighter flame, owing to an increased rate of chemical action, and at last we shall reach a point where it is possible to cut off the electric current without causing at the same time the extinction of the flame. This is the true temperature of ignition, the temperature at which the reaction proceeds at a rate just sufficient to overbalance the loss of heat by radiation, conduction, and convection from the burning layer of gases, so that the next layer is put in the same state, and steady combustion proceeds.

Phosphorescence has been spoken of as degraded combustion, and, though literally the appellation is correct, I think it is liable to be misunderstood. Again, it is often supposed that phosphorescence is necessarily associated with the formation of incompletely oxidised products. This may be the case in a chemical system which is capable of affording different products at different temperatures, but it is not an essential feature; the phosphorescent combustion of sulphur, for example, affords nothing but sulphur dioxide.

Temperature of ignition is, then, neither a temperature at which combination suddenly begins nor one dependent solely on the nature of the combining gases. It will vary with the proportion in which the gases are mixed and with their pressure and other circumstances. Notwithstanding the simplicity of this conception, it must be admitted that there are many obscure facts connected with the ignition of gases. The inflammability of gaseous mixtures is not necessarily greatest when they are mixed in the proportions theoretically required for complete combination; the influence of foreign gases does not appear to follow any simple law; the presence of a very small quantity of a foreign gas may exercise a profound influence on the ignition temperature as in the case of the addition of ethylene to hydrogen. When a mixture of methane and air is raised to its ignition temperature, a sensible interval (about ten seconds) elapses before inflammation occurs. These facts are cognate to others which have increased upon us so abundantly in connection with the influence of moisture on chemical change. The study of the oxidation of phosphorus in particular brings us among rocks and shoals. Apart from the influence of moisture on the combination we have the limitation of the process by a certain tension of oxygen and by minute quantities of a vast number of chemical substances, among which, in spite of much labour, no other common bond can be found. We do not know what oxide is initially formed in the oxidation, and the existence of the oxides P_4O and P_2O is as confidently disputed as it is affirmed. There is some reason for believing that the phosphorescence connected with phosphorus succeeds the formation of one oxide and accompanies the formation of another. The state of the oxygen, whether atomic, ionic, or molecular, which acts on phosphorus, the induced oxidation of other substances, the ionisation of air accompanying the oxidation—these are all matters concerning which there exists a bewildering literature that hangs over us like a cloud. The whole of my Address would, in fact, not suffice for a summary of the state of our ignorance about the oxidation of phosphorus. The subject, simple as it appears at first sight, is really involved with a vast number of unsolved chemical problems the elucidation of which would throw much light on chemical action in general. I may, perhaps, bequeath the topic to some successor in this Chair as one which may serve to illustrate the advance of knowledge since these present days of darkness.

The structure of flames has always been regarded as dependent upon the chemical changes taking place in the differentiated regions, but until recent times little attention has been given to any question beyond the cause of the bright luminosity of hydrocarbon flames. In a flame such as that of hydrogen or carbon monoxide, where we have some reason to suppose that the same kind of chemical transaction is taking place throughout the region of combustion, we should not expect to find a differentiation of structure, and, as a matter of fact, we do not find any. Erroneous ideas have gained currency from the use of impure gases, and hydrogen is still described as burning with a pale blue flame, although Stas long ago stated that if the gas is highly purified, and the air freed from dust, the flame even in a dark room can only be discovered by feeling for it; a fact consistent with the line spectrum of water lying wholly in the ultra-violet. The presence of a very small quantity of free oxygen in carbon monoxide destroys the perfect simplicity of the single shell of blue flame with which the purified gas burns, and in other flames small quantities of gaseous impurities or of atmospheric dust give rise to features of structure and halos which have been frequently supposed to pertain to the flame of the combining gases. The fringe of a flame in air may be often tinged by the presence of oxides of nitrogen.

No flame better illustrates the relation of structure to chemical processes than that of cyanogen, where the two steps in the oxidation of the carbon are clearly marked out in colour. Apart from hydrocarbon flames, very few others have been carefully explored from this point of view. There is, unfortunately, no gas composed of two combustible gaseous elements; and, though such gases as the hydrides of phosphorus and sulphur do not fall far short of this, the experimental difficulties of an exact exploration of their flames are very great. We are thus prevented from studying the flame of a composite combustible in its simplest form.

The flames of hydrocarbons have naturally been the subject of most frequent investigation. The use of single hydrocarbons instead of the mixtures present in coal-gas and other common combustibles has simplified the study considerably. Two problems stand out prominently: one is to trace the steps in the oxidation of the hydrocarbon, the other to account for the bright patch of yellow luminosity. With regard to the question of the luminosity, I do not think there is any longer doubt about its being due essentially to the separation within the flame of minute solid particles of what is practically carbon. The separation seems to be adequately explained by the high temperature of the blue burning walls of the flame, which decomposes the unburned hydrocarbon within. In a similar way arsenic and sulphur and phosphorus are liberated within flames of their hydrides; but these elements, being volatile, do not appear as solids unless a cold object be placed within the flame. In the case of the hydride of silicon the liberated element at once oxidises to form the solid non-volatile oxide, which gives a bright glow.

The mode in which a hydrocarbon yields carbon by the application of a high temperature has been the subject of

experiment and of hypothesis; but neither the view of Berthelot, that the carbon results from a continuous coalescence of hydrocarbon molecules with elimination of hydrogen, nor that of Lewes, according to which the formation and sudden decomposition of acetylene is the essence of the phenomenon, appears to me to be in harmony with the experimental facts; and I am not aware that either view has secured any support from other workers in this field. It is certainly not easy to ascertain experimentally the changes undergone by a single hydrocarbon as its temperature is raised, and at the last it may be objected that the course of events in contact with the solid walls of a containing vessel is not necessarily the same as that within the gaseous envelope of a flame. I am glad to think that there is promise of further light on this subject from the work of Professor Bone.

The course of oxidation of hydrocarbons has been the subject of very careful and fruitful study. The old view that a selective or preferential oxidation of the hydrogen always took place, that with a restricted supply of oxygen the hydrogen was oxidised and the carbon set free, is, I think, no longer maintained by anyone who has studied the question. The explosion of ethylene with its own volume of oxygen, which leaves us with practically all the carbon oxidised and all the hydrogen free, is fatal to this view. Again, when hydrocarbons are burned in a flame with a restricted supply of air, as is the case in the inner cone of the flame of a well-aërated Bunsen burner, there is clearly no separation of solid carbon, and the products of combustion when withdrawn and analysed disclose the presence of much free hydrogen and no unoxidised carbon. In describing this experimental fact I have spoken of it as the preferential oxidation of carbon. I have always thought it pedantic to quarrel with that expression; for, in speaking of a chemical transaction, we usually include only a description of the initial and final states of combination. I should be sorry, however, to detach the expression from the facts it describes and to exalt it into a general doctrine. That would be quite inadmissible, and, if there is any danger of misunderstanding, it would be better to avoid using the expression.

The admirable researches carried out in the University of Manchester by Professor Bone and his collaborators have afforded most valuable information as to the oxidation of hydrocarbons at temperatures extending from those of incipient oxidation up to the highest ones that prevail in a flame. According to Professor Bone, the oxidation of a hydrocarbon involves nothing in the nature of a selective or preferential oxidation of the carbon or the hydrogen; but it occurs in several well-defined stages, during which oxygen enters into and is incorporated with the hydrocarbon molecule, forming oxygenated intermediate products, among which are alcohols and aldehydes. The reaction, just referred to, between ethylene and an equal volume of oxygen is, according to Professor Bone, to be represented by the scheme:—

$$\begin{array}{ccccccc} CH_2 & & CH.OH & & CH.OH & & H_2C{:}O \\ \| & \rightarrow & | & \rightarrow & | & \rightarrow & \\ CH_2 & & CH_2 & & CH.OH & & H_2C{:}O \end{array} \qquad \begin{array}{c} \\ \rightarrow \\ \\ \rightarrow \end{array} \qquad \begin{array}{c} H_2+CO \\ \\ H_2+CO \end{array}$$

There can be no question about the facts on which this scheme is based, and they are a new and important addition to knowledge.

It is a great aid to the study of chemical changes, when we can resolve them into stages, whether or not these stages be realisable under certain experimental conditions. In this way we can get a clear view of the relationship between the action under one set of circumstances to the action under another set; and in this way also we can often establish rational links between reactions which at first sight seem quite disconnected. Intermediate reactions are much used to elucidate cases of contact action, and in the processes of organic chemistry they are almost universally assumed.

I am far from wishing to disparage these practices, but I think it important that we should realise how far we are dealing with convenient devices, and how far with ascertained facts. The isolation of an intermediate product under one set of circumstances is in itself no proof that this product is transitorily formed when the reaction is proceeding under another set of circumstances; and if we were to assume generally that because we can represent a chemical transaction as if it were due to a successive construction and destruction of a series of molecular edifices it actually does take such a course, we should, I think, be making the same kind of mistake as to suppose that in the application of two differently directed forces to a body at rest, the body will move successively in the direction of each force instead of moving immediately in the direction of their resultant. I know that I may be considered hypercritical, and perhaps obstinate, in this matter; but I wished to state the reasons that prevent me from accepting entirely the interpretation which Professor Bone has given to his experimental results, and to draw attention to a question of general importance that has not, I think, received the attention it deserves.

The mode of burning of carbon, whether in the free state or as a constituent of a compound, is not at all easy to determine; and notwithstanding many investigations, among which must be specially mentioned those of Professor H. B. Dixon and his collaborators, so simple-looking a question as whether carbon forms carbon monoxide by directly uniting with oxygen, or only by reducing carbon dioxide, is still a matter of uncertainty.

Our knowledge concerning the question of flame temperatures has been much improved in recent times, thanks mainly to the admirable work of M. Le Chatelier. The well-known memoir of Mallard and Le Chatelier on the explosion of gases supplied the data which first permitted of a moderately exact calculation of flame temperatures, and the perfection of the thermo-couple by M. Le Chatelier gave us the first instrument that could be used directly for making a satisfactory measurement. The uncertainty connected with this subject may be well illustrated by quoting the temperatures that have at different times been ascribed to the flame of coal-gas when burnt in a Bunsen burner, where we have had values varying from 1230° to 2350° C.

The question of calculating the temperature attained during combustion by reference to calorimetric values, specific heat, dissociation, and other considerations is to form the subject of a joint discussion with Section G during the present meeting, so that I shall not here enlarge upon it.

With regard to the use of thermo-couples, I may remark that the practical difficulties have been successfully met. The chief difficulty is, of course, to secure that the thermo-junction attains as nearly as possible the temperature of the region in which it is immersed. As ordinary flames consist of thin shells of burning gases, on either side of which there is a very rapid fall of temperature, it is necessary to use thin wires, and to dispose them so that there is no appreciable drain of heat from the junction. By using wires of different gauge for the couples it is possible by extrapolation to arrive at a temperature for a couple of infinitely small cross-section, and it is also possible to make a correction for the superior radiating power of the couple as compared with the flame-gases. Without this last correction a maximum temperature of 1770° was obtained for the Bunsen flame by Waggener in Germany, and 1780° by White and Traver in America. Correcting for radiation, Berkenbusch found 1830° as the maximum temperature.

M. Féry, by an ingenious application of his beautiful optical pyrometer to a flame containing sodium, gives 1871° as the highest temperature of the flame of a Bunsen burner burning coal-gas.

The consideration of flame-temperatures has become of increasing importance in the arts owing to the use of the Welsbach mantle as a means of deriving light from coal-gas. The great improvements which have been made in the efficiency of atmospheric burners depend primarily on the fact that the smaller the external surface we can give

to a flame consuming gas at a fixed rate, the higher must be the average temperature; and since the emission of light from a mantle is proportional to a high power of the absolute temperature, a small increase of temperature is of great effect on luminosity.

The acetylene-oxygen flame in which a temperature of about 3500° prevails, not very different from that of the electric arc, is the hottest of the hydrocarbon flames, and finds some important practical uses.

I have already said something about the luminosity of flames so far as relates to the separation and glow of solid carbon. But there remains the more general question of the luminosity of flames containing nothing but gases. The older explanation of the emission of light from combining gases said no more than that the energy liberated during the reaction and appearing as heat raised the product to incandescence—that is to say, so increased the velocity of its molecules and the violence of their collisions that vibrations were set up whose wave-lengths lay within the limits of visible radiation. This explanation has long been questioned, and there is now, I think, a very general agreement that it will not suffice. The average temperature, in fact, prevailing in a flame, if attained in the product of combustion by the supply of heat from outside, does not suffice to make that substance luminous. We are therefore thrown back upon the conclusion that the generation of light in a flame is not a consequence, though it is an accompaniment, of the elevation of temperature. The question now is, Can we go any further? To do this we are led to consider individual molecular transactions instead of statistical averages, and the view presents itself that the combining atoms may, in losing their chemical energy, form directly systems of independent vibration where the radiation is such as to fall within the limits of visibility. If we picture such vibrating systems momentarily formed, it is easy to see that by their collision one with another they may acquire in a secondary way increased translational motion, and so lead to a state of things where the greater part of their energy is degraded in the form of heat. The high temperature of a flame would then be a consequence rather than a cause of its light.

This subject of the mechanism of luminosity, however, like so many others, has now become involved with the theory of electrons, and a chemist may be excused if he hesitates to pursue the subject further. Some years ago I called attention to the scantiness of our knowledge of the chemical changes that take place when metallic salts are used in flames for the production of spectra. Though there was general agreement that, for example, the yellow flame produced by common salt was due to the liberation and glow of metallic sodium, there was no agreement as to how the sodium was set free.

Arrhenius, pursuing the analogy which exists between the laws governing matter in the gaseous state and in the state of dilute solution, had previously been led to the view that the electrical conductivity of flames containing salt-vapours was due to ionisation of the salt throughout the volume of the flame. It appeared possible therefore that the luminosity might be ascribed likewise to the metal separated in the ionic state. Experimental investigation undertaken with a view to elicit information on this subject seemed to favour the view that the metal was reduced by chemical processes, and that it glowed in the un-ionised condition. Evidence seemed to point to the conclusion that, for example, when common salt is introduced into the flame of coal-gas the sodium chloride yields sodium by the conjoint action of steam and reducing gases; when liberation of the metal was prevented by adding a large quantity of hydrochloric acid to the flame the glow disappeared, but the conductivity was not always diminished. The fact that sodium salts, including the chloride, impart their characteristic glow to the flame of cyanogen and to other flames in which water is absent leads to some difficulty in finding a chemical explanation, and it must be admitted that a direct thermal dissociation of an alkaline halide or oxide is not out of the question. The interval of detachment of the metallic atom may be exceedingly brief, but it must be remembered that even so short a time as the interval between the molecular encounters in a gas at a high temperature is still sufficient for the emission of thousands of undisturbed characteristic vibrations. The experiments to which I have alluded have been followed up with great industry and success by Professor H. A. Wilson, who has added much to our knowledge of the electrical condition of the flames containing vaporised salts; but the question of the condition of the luminous gas is still far from being settled. Very interesting and important investigations have been carried out by Lenard, who has shown that the stream of luminous vapour produced from a sodium salt in a Bunsen flame is deflected in an electric field in such a way as to indicate that the vapour is positively charged; but he gives reason for believing that the charged condition is intermittent with the neutral condition. The lines in the spectrum of an alkali metal are divisible, as is well known, into distinct groups or series, in each of which the oscillation frequencies corresponding with the lines are in a definite mathematical relationship. The principal series, which include the lines seen individually as such in ordinary flame spectra, are, according to Lenard, due to the electrically neutral atoms. In a salted spirit flame, and in other flames of low temperature where only lines of the principal series are represented, the stream of luminous gas does not behave in an electric field as if it were charged. In the flame of coal-gas burnt in a Bunsen burner the salt-vapour gives, in addition to the distinct lines of the principal series, diffuse bands of luminosity on the dark background, which, according to Lenard, represent the undeveloped subordinate series; and it is the atoms emitting these series that are deflected in the electric field. It is inferred therefore that the light in a salted Bunsen flame comes from different groups of centres of emission—the principal series from the neutral atom, and the lines of the first, second, and third subordinate series from atoms which have lost respectively one, two, and three electrons. Lenard goes further, and shows that the salt-vapour in a Bunsen flame, as in the flame of the electric arc, emits these different kinds of radiation from different structural regions; thus the vapour at the edge of the flame is electrically neutral, and gives only the lines of a principal series.

The negative electricity in a salted flame would, according to Lenard, be disembodied, and recent experiments by Gold confirm the view that the negative carrier in flames is a free electron. In connection with this subject I ought to allude to an investigation by Tufts, which seems to throw some doubt on the conclusions which were drawn from the experiments made by Professor Wilson, Dr. Dawson, and myself; and I must also mention an important contribution to the subject recently made by Professor Hartley, in which considerable light is thrown upon the chemical changes undergone by compounds of the alkaline earth metals when they are introduced into flames, and upon the relation of these changes to the various spectral features. I am afraid, however, that it would be wearisome if I were to prolong this summary, and I must be content to leave it without doing justice to those who are engaged upon the work. The subject is obviously one of fundamental importance in relation to spectrum analysis, and my own slight connection with it has only strengthened my opinion that there is still a great deal connected with the genesis of spectra that requires the attention of the chemist even more than that of the physicist. Spectrum analysis arose under the joint influence of Bunsen and Kirchhoff, and I think its problems still call for more combined work on the part of chemist and physicist than has latterly been the custom.

Having given a short summary of the present state of knowledge on one particular chemical topic, I may perhaps be permitted to conclude my Address with a few general observations relating to the science as a whole.

The contemplation of such a life as that of Berthelot

makes us realise in a vivid way the progress of chemical science. He was a chemist without limitation, his activity extending over the whole range of the science, physical, inorganic, and organic. Whilst we must not forget his exceptional powers, we cannot help feeling how different in its extent was our science when he entered upon his labours from what it was when they ceased, and we cannot help feeling how vain it now is for anyone to hope for so imperial a sway.

Yet it is difficult to believe that the state of chemistry can ever have been more interesting than it is at the present moment, or that anyone who sighs for the good old times can do so from anything but the love of a quieter life. We need not go back more than twenty years to find a sharp contrast. At that time there was indeed no want of activity, but it was that of a band of travellers who had left their frontier adventures far behind, and were marching steadily over a wide and almost uninterrupted plain. To-day we are among the mountains, with new peaks and prospects appearing on every side. Truly a steady head is required; and well may we ask, Whither are we going and where is the path of progress and of safety? I rejoice to live in such times; but I feel no competence to describe them, still less can I pretend to have vision keen and comprehensive enough to let me figure as a guide.

One of the penalties of devotion to a progressive science is the constant feeling of being left behind, and the knowledge that, while we are attending to our personal task, things are happening, near or far, that may, for all we know, be affecting the simplest facts and the most elementary principles on which we have been accustomed to rely. This is a feeling that may well prevail at the present day. At the same time I do not think there is any occasion for panic, and I cannot help regretting the somewhat sensational language that has been used, even within our own circles, in regard to recent discoveries. The revelations attendant upon the investigation of radio-activity do indeed mark a distinct epoch in the history of chemical discovery, but that they entail anything like an unsettlement of our scientific articles of faith is not to be admitted for a moment. They make us realise in perhaps a not unprofitable way that scientific knowledge and scientific theories are necessarily proximate, never ultimate, and that ideas which may have been entertained for a long time without modification, and so have begun to seem perpetual, are, after all, only provisional.

There is certainly some embarrassment on finding that a substance like radium, which according to the conventions would be called a chemical element, breaks up so as to give substances which, according to the same conventions, are likewise called elements. But the confusion is one of terminology and not of ideas. I think it likely that few chemists of my own generation have been in the habit of regarding the conventional elements as the ultimate compositional units of matter. We know that in our own country distinguished men of science like Sir William Crookes and Sir Norman Lockyer have always insisted on the complex nature of the elements, and I suspect there are many among us who might own to having made sober, if unsuccessful, attempts at the resolution of elements before the days of radium.

The perplexities of chemists at the present day do not come, I think, from the novelty of the ideas that are being presented to them, but from the great rapidity with which the whole science is growing, from the invasion of chemistry by mathematics, and, in particular, from the sudden appearance of the subject of radio-activity with its new methods, new instruments, and especially with its accompaniment of speculative philosophy. There is an uneasy feeling that developments of great importance to the chemists are being made by experiments on quantities of matter of almost inconceivable minuteness. Spectrum analysis of course took chemistry beyond the limits of the balance, but the new materials which it disclosed could at least be accumulated in palpable quantity. With radio-activity we seem, in relation to the ponderable, almost to be creating a chemistry of phantoms, and this reduction in the amount of experimental materials, associated as it is with an exuberance of mathematical speculation of the most bewildering kind concerning the nature, or perhaps I should say the want of nature, of matter, is calculated to perturb a stolid and earthy philosopher whose business has been hitherto confined to comparatively gross quantities of materials, and to a restricted number of crude mechanical ideas. He is tempted to think of Falstaff's reckoning, and to explain with Prince Henry, "Oh, monstrous! but one halfpennyworth of bread to this intolerable deal of sack!" Experimental science has latterly been spun to greater and greater fineness, until in the region of the N-rays the objective element seems to have disappeared altogether.

I should, however, gravely abuse the position in which I am allowed to speak for the moment as a representative of chemists if I failed to express profound admiration for the masterly work which has been accomplished by the pioneers of the science of radio-activity. All that I wish to say beyond that, is in explanation of a certain awe or trepidation which chemists of the older school may feel in the presence of such bold explorers; and I am the more tempted to say something on the subject, because in recent times, before the advent of radium, a good deal has happened which has given chemists occasion to ask themselves whether chemistry was not beginning, as it were, to drift away from them.

The most conspicuous development of the science during the past twenty years has been, of course, on the physical side, and abundant have been its fruits; but it has seemed to demand from chemists habits and endowments which they did not normally possess, and which they could not easily acquire. I was much struck by a remark made to me a few years ago by a distinguished chemist, who is, I think, the most perfect manipulator I have ever seen at work, to the effect that he felt himself submerged and perishing in the great tide of physical chemistry which was rolling up into our laboratories. Now, it is precisely such men that must be preserved to chemistry. Though chemistry and physics meet and blend, there is, I believe, an essential difference between the genius of the chemist and the genius of the physicist, and I venture to think that some insistence on the primary functions of a chemist is not untimely. The chemist's first qualification is that he shall be master of a peculiar craft; his greatest merit that he is a consummate workman; his distinctive power a nicety of discrimination in questions affecting the composition and quantity of materials. He is not given to elaborate theories, and is usually averse to speculation; nor has he usually an aptitude for mathematics. Such the normal chemist is, or was, and such I hope he always may be—naked perhaps in some respects, but unashamed.

There seems to be a solicitude in some quarters to make a chemist something more than a chemist, a solicitude which, if gratified, will, I believe, make him something less than one. We are told, for example, that a chemist should be a mathematician. I do not admit it for a moment. Some mathematics he must of necessity have—that has always been admitted—but in proportion as chemistry develops on the mathematical side does it become important, not that our chemists should be trained in mathematics, but that they should be more than ever carefully trained in the art of exact experiment; that their methods of work, their powers of observation, and, if possible, their experimental conscience, if I may use the expression, should acquire a finer edge. There is never more cause for anxiety than when we see a mathematical theory awaiting the delivery of the confirmatory facts, and there is nothing more important for chemistry than the continual recruiting of that old guard which will be ever ready to stand to arms on the appearance of an eager theorist.

I do not for a moment wish to disparage the adventurous spirits within or outside our science, still less do I wish to range myself with those who meet new ideas with

mere objurgation or raillery. We must be content to see new alliances and new activities on the frontiers that separate us from other sciences; content to see many new kinds of chemistry arise in which we cannot all effectually participate. Chemistry is becoming bewildering in its extent, and it would be a great misfortune if this led to the notion that every chemist must try to enlarge his ambit to its confines and fit himself for every variety of work. Those of us who have responsibilities as teachers cannot, I think, be too careful, lest in the attempt to secure breadth we may encourage shallowness and fail to give our students that peculiar and time-honoured discipline in exactitude of work in chemistry proper, which has characterised the chemists of the past, and which is infinitely more important than superficial dealings with a great variety of processes and appliances. I confess that I have frequent misgivings as to whether our modern courses of instruction may not tend to turn out chemists more learned in the science and less perfect in the art than was the case under the ancient *régime*. There was, after all, great virtue in the system which often detained a student day after day, or perhaps week after week, on a single problem of chemical composition such as is involved in the exact analysis of fahl-ore. It is not easy to meet all requirements, but I think we shall all agree that, whatever is left undone, we must make a chemist a good craftsman. It is of the utmost importance that those whom we send out to work in the newer fields shall take with them the resources that have proved most serviceable in the old, and I think it is by supplying such men for special service, rather than by attempting to shift the centre of gravity of the whole system of chemical education, that we can best serve the newer interests.

Another perturbation within the chemical camp in recent times has come from the region of philosophy. Even before the days of radium we have been accused of clinging too fondly to our atomic theory and of stating our knowledge too exclusively in terms of that theory. We are said to have drifted into a dogmatism as real as any we ourselves have had to attack, and to shut our eyes to the light which will enable us to orient ourselves truly in the wide realm of thought. The answer that most of us would give would be, that we value our hypotheses according to their productiveness in new knowledge, and that it is, on the whole, perhaps better to over-exalt an hypothesis that is fertile than from high considerations of philosophy to allow our ideas to become so fluid that they can afford no rigid framework for thought. I think that the attempts to view chemical phenomena apart from the atomic hypothesis, interesting as they undoubtedly are, have not made us feel that this hypothesis has either misled us in any matter of fact or obscured any pathway that we might have followed with greater profit. The value of the thermo-dynamical treatment of chemical problems is attested by its fruitfulness in promoting fresh discoveries; and here we may welcome a valuable adjunct to the atomic hypothesis. But I do not think we are called upon to acclaim a new method of treating old questions unless it promises some more tangible result than an alleged improvement of our intellectual morals.

If, as I have ventured to hint, mathematics brings with it an element of danger into chemistry, I think that the intrusion of metaphysics would give far greater cause for apprehension. Philosophy always stands with open arms desiring a closer embrace of all the sciences, of which she declares herself to be the fond mother, whilst Science, as we understand the term, has stood reluctant, suggesting, as someone has wittily remarked, that she regards Philosophy rather as a mother-in-law. It may perhaps be desirable, especially in the present state of things, that scientific men should allow themselves to become a little more interested in deep questions affecting all knowledge, and should at least examine with some care the gifts that Philosophy is so anxious to bestow upon us. I have a fear that otherwise in the elaboration of scientific theory we may find ourselves embroiled in an unequal contest with what I cannot but regard as the traditional enemy—I mean the unmitigated metaphysician—and the suggestion that I make is, to tell the truth, not so much from the hope of gain as from the desire for self-defence and the safe preservation of the methods that have served us so well in the past.

I think the accusation that we delude ourselves into the belief that our hypotheses are final truth is not true of any thoughtful chemist; the great men of science have surely possessed that quality of mind which philosophy would most approve. If, as has often been remarked, Faraday was mathematically-minded, though untrained in mathematics, it seems not less true that he stood in the same relation to philosophy. When, for example, he was asked to express his opinions on the atomic theory, he wrote as follows:—

"I do not know that I am unorthodox as respects the atomic hypothesis. I believe in matter and its atoms as freely as most people—at least I think so. As to the little solid particles, which are by some supposed to exist independent of the forces of matter, and which in different substances are imagined to have different amounts of these forces associated with, or conferred upon, them (and which even in the same substance, when in the solid, liquid, and gaseous state, are supposed to have like different proportions of these powers), as I cannot form any idea of them apart from the forces, so I neither admit nor deny them. They do not afford me the least help in my endeavour to form an idea of a particle of matter. On the contrary, they greatly embarrass me; for after taking account of all the properties of matter, and allowing in my consideration for them, then these nuclei remain on the mind, and I cannot tell what to do with them. The notion of a solid nucleus without properties is a natural figure or stepping-stone to the mind at its first entrance on the consideration of natural phenomena; but when it has become instructed, the like notion of a solid nucleus, apart from the repulsion, which gives our only notion of solidity, or the gravity, which gives our notion of weight, is to me too difficult for comprehension; and so the notion becomes to me hypothetical, and, what is more, a very clumsy hypothesis. At that point, then, I reserve my mind as I feel bound to do in hundreds of other cases in natural knowledge."

This is the attitude of mind, I think, of all thoughtful chemists; if they do not exhibit it ostentatiously it is only because it is as disturbing to the proper work of a chemist for him to be constantly dwelling on the inward nature of his hypotheses as it is distracting in ordinary life to have men always talking about their emotions.

Few, I think, will deny that the atomic theory stands to-day as an indispensable instrument for productive chemical work; it has neither had its day nor ceased to be. Physicists have never been quite satisfied with the hard invisible ball of specific substance and definite mass which has served chemistry so well. They have given it bells, have made a vortex ring of it, and have indeed done much that few chemists can understand to make it meet the exacting requirements of their science. But to us it has always been the same; what we have done to it has been external; we have given it, vaguely perhaps, a charge of electricity, a store of energy; we have attached the hooks or rods of valency, but we have not meddled with its interior. We are now called upon by chemical considerations of change of composition, as well as by other considerations more recondite, to subdivide our atom, to credit it with an unsuspected store of energy, to consider it a congeries of unsubstantial electrons. We should wish, of course, to know that the evidence is good enough, but otherwise there can be no possible objection from our side; it will undo nothing that has been done, and we may have good hopes that it will lead to the doing of many new things in chemistry. The newer theories are in consonance with the old in one most vital point; they afford those mental pictures of phenomena which most of us find indispensable for fruitful work. They do not belong to what Professor Schuster has characterised as "the evasive

school of philosophy." "Those," he says, "who believe in the possibility of a mechanical conception of the universe, and are not willing to abandon the methods which from the time of Galileo and Newton have uniformly and exclusively led to success, must look with the gravest concern on a growing school of scientific thought which rests content with equations correctly representing numerical relationships between different phenomena, even though no precise meaning can be attached to the symbols used." Most of us, I think, will take comfort in this pronouncement and rejoice that if our conception of the atom is to be transformed, it may still be represented as having some kinship with what Sir Henry Roscoe's famous examinee described as the "square blocks of wood invented by Dr. Dalton."

CORRESPONDENCE.

THE NITROGEN GROUP OF ELEMENTS.

To the Editor of the Chemical News.

Sir,—In past communications to the Chemical News I have drawn attention to thermo-chemical equivalence.

By grouping the elements, we find that the nitrogen group contains a similar relationship to that already shown as regards those elements we have considered individually, and that they also have a group relationship pointing to—if the theory is fully carried out—a more complete comprehension of the nature of these elements than that arrived at by the atomic theory.

The data at hand show that the oxides and chlorides at once give the necessary relations for supporting the belief in the thermo-chemical equivalents of the elements already treated. They also show that in these equivalents of similarly grouped elements, as applied at any rate to the nitrogen group, these equivalents are approximately simple multiples of one another, such as 2, 3, &c.

Finally, where apparently utter discrepancy occurs in such thermo-chemical relations, they may still be shown to point to a confirmation of the views already stated if considered dynamically.—I am, &c.,

J. C. Thomlinson.

NOTICES OF BOOKS.

Stereochemistry. By A. W. Stewart, D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

The author of this text-book may be congratulated upon the production of a work which students of physical chemistry will find of the utmost value. It is written in remarkably clear language, such as too often does not appear to be at the command of a writer of deep knowledge, and no mass of detail is allowed to obscure the main issues. The book is divided into two sections. The first deals with stereoisomerism, firstly when it is accompanied by optical activity, and in the second place the numerous cases of stereoisomerism without activity are discussed. The second section deals with stereochemical problems into which isomerism does not enter, and includes a full account of the most important researches connected with the phenomena of steric hindrance. The reader who is not specially interested in this branch, and who thus requires only a general knowledge of the principles involved, is advised to omit certain pages, and to read only the summaries which have been carefully written for his special benefit. The relations between space formula and chemical properties, and the effects of substitution upon stability are also considered in this part of the book; in the course of an admirable discussion of the various space formulæ, which have been proposed for the benzene molecule, the author expresses the opinion that Collie's formula is superior to all others, and that in essentials it is correct. In an appendix full directions for the construction of models to illustrate stereochemistry, and information as to where ready-made sets can be procured, are given. The value of the book lies, perhaps not so much in the vast amount of material it contains nor even the care with which this has been selected and arranged, but more particularly in the constant allusions to unsolved problems, to discrepancies, still unexplained, between facts and current theories, and to the directions in which fruitful research may be prosecuted. The admirable summaries throughout the text will do much to clear away the difficulties of the subject and to help the reader to get a firm grasp of the main principles of stereochemistry.

Peat: Its Use and Manufacture. By Philip R. Björling and Frederick T. Gissing. London: Charles Griffin and Co., Ltd. 1907.

This book gives a short and interesting account of the uses of peat for all purposes, special stress being laid upon its importance as fuel. As an introduction to larger works upon the subject it will be found excellent, being clearly written and well illustrated. The problem of the drying of peat by air, artificial heat, and pressure is considered at some length, and the objections to existing processes are carefully explained; tables of the ultimate analysis of peats from all parts of the world are included, and the manufacture of peat fuel by the more commonly employed processes is described and illustrated. Its uses as fuel, its special requirements in the way of fire-grates, &c., in order that it may burn satisfactorily, and its uses otherwise than as fuel form the subjects of the last two chapters, in the former of which especially much valuable information as to tests and results is contained.

Séance Solennelle de Distribution des Prix de Concours. ("Meeting for the Distribution of the Competitive Prizes"). Geneva: W. Kündig et Fils. 1907.

This number of the Reports of the University of Geneva contains a short biographical notice of Sir Humphry Davy, who died in Geneva in 1829, and in whose memory the Davy prize was founded by his widow. The professor of theoretical and technical chemistry at the University, Philippe A. Guye, delivered the lecture which is reprinted here, and which contains a generous appreciation of Davy's scientific work. The volume also includes a list of the students upon whom degrees were conferred in 1906, together with the reports of the Rector and Juries appointed to decide the awards of the various prizes offered by the University.

Quarterly Journal of the Institute of Commercial Research in the Tropics. Liverpool University. Vol. II., No. 4. Liverpool: The Offices of the Institute. London: Williams and Norgate. 1907.

The fourth number of Volume II. of this journal contains outlined accounts of the various expeditions which have been dispatched by the Institute to European countries and to the United States to study the working of similar institutions, as well as to West Africa, to investigate more especially problems connected with rubber, cocoa, fibre, and maize. During these West African expeditions a large quantity of valuable botanical and entomological material was collected, and the Institute has also to chronicle important commercial results in the way of improvement of produce, effected by native farmers who have followed the instructions given by the Institute's representatives. The journal contains articles describing the

analysis of various tropical products, among which special attention must be called to the paper by the chief chemist, Dr. Spence, on the chemical nature of the resinous substances always found in crude rubber coagulated by the usual methods from latex, and upon possible means of improving inferior rubber containing a large proportion of these resinous substances. The report shows that the assistants at the Institute are devoting their energies to its service with remarkable enthusiasm, and are doing work which will be of material benefit to the development of the resources of tropical regions.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 1, July 1, 1907.

Direct Hydrogenation of the Anhydrides of Aliphatic Acids.—Paul Sabatier and A. Mailhe.—The hydrogenation of anhydrides in presence of reduced nickel leads to a splitting of the molecule into aldehyde and acetic acid. Thus, with acetic acid anhydride the reaction is $\frac{CH_3.CO}{CH_3.CO}>O + H_2 = CH_3.CO.H + CH_3.CO.OH$. Then the greater part of the aldehyde is itself hydrogenated, giving ethyl alcohol, which is partially etherified by the vapours of acetic acid, giving water and ethyl acetate, $\frac{CH_3.CH_2}{CH_3.CO}>O$. The water thus formed transforms some of the acetic anhydride into acid. It is noteworthy that the nickel is not affected by the acetic acid generated. With other anhydrides the principal reaction is in all cases the splitting of the molecule into acid and aldehyde, the hydrogenation of which yields the corresponding alcohol. A certain amount of ether salt, $\frac{R.CO}{R.CH_2}>O$, results from the alcohol and acid formed during the reaction. The amount of ether salt decreases as the amount of carbon in the anhydride increases. Reduced copper at 200—210° acts like nickel, but is less active, and when it is used the proportion of alcohol formed, and therefore of ether salt, is much less. The copper is itself much more rapidly affected by the reaction than nickel.

Synthesis of Secondary Isoamyl Alcohol, $(CH_3)_2=CH-CH(OH)-CH_3$. — Louis Henry. — The oxide of isobutylene, $(CH_3)_2=C\begin{array}{l}-CH_2\\ \diagdown O\diagup\end{array}$, reacts with a magnesium organic compound in the same way as its isomer, isobutyric aldehyde, and the author is inclined to think that it is converted into this isomer, or at any rate it undergoes some atomic transformation. When monochloracetone acts on two molecules of methyl-magnesium bromide the complex $CH_3>C(O.MgBr)-CH_2Cl$ is formed. Under the influence of heat this gives Cl.MgBr and isobutylene oxide, which is converted into the secondary alcohol, $(CH_3)_2=CH-CH(OH)-CH_3$, by the further action of the methyl-magnesium bromide. The author has no doubt that ethyl monochloracetate, $ClCH_2-CO(OC_2H_5)$, with three molecules of the magnesium compound would yield secondary isoamyl alcohol, but he has not yet investigated this point. When monochloracetyl chloride, $ClCH_2-COCl$, acts on three molecules of methyl magnesium bromide a violent reaction occurs, and an appreciable quantity of secondary isoamyl alcohol is formed.

Absolute Atomic Weight of Chlorine.—G. D. Hinrichs.—If Ag = 108, Cl = 35·5, the ratio AgCl : Ag is 1·32870. The change for Ag = −30, for Cl = +93; variations for Ag = 3⅓, for Cl = 107. When the figures obtained by different investigators from Berzelius (1820) to Richards (1905) are examined, it is found that the excess in the fifth place of decimals has been reduced, by perfecting the method, from −85 to −3. Since this excess represents milligrammes in 100 grms. of silver the agreement of the later experiments with the theory of absolute atomic weights is remarkable, and the author adduces this agreement as an argument in favour of the perfect commensurability of the atomic weights of silver and chlorine.

Determination of Phosphorous Acid.—C. Marie and A. Lucas.—To determine phosphorous acid by permanganate in alkaline solution, a known volume of standard permanganate is warmed with potassium carbonate, and the phosphorous acid introduced into it. A brown precipitate of dioxide is at once formed. It is left for about fifteen minutes at 80°, and then a known volume of strongly acid solution of Mohr's salt is added. The precipitate at once dissolves, and the excess of ferrous salt is titrated by means of the solution of permanganate. It is best to determine the ratio of the two solutions (Mohr's salt and permanganate) by a blank experiment carried out under the same conditions. The strength of the permanganate can be determined by the usual methods, but it is preferable to use a substance which can be oxidised in an alkaline medium. Calcium formate is very suitable for this purpose. The equation is—

$$4KMnO_4 + 3Ca(CO_2H)_2 = 4MnO_2 + 3CaCO_3 + K_2CO_3 + 2KHCO_3 + 2H_2O.$$

Phosphites and hypophosphites which are readily oxidised to phosphites can be determined by this method.

Action of Chlorine and Sulphur Chloride on some Oxides.—F. Bourion.—When chlorine and sulphur chloride act simultaneously on zirconium oxide heated to a red heat crystals of $ZrCl_4$ are formed. These crystals retain some sulphur chloride, but may be purified by cooling them in a current of chlorine or subliming them in a current of hydrogen or dry chlorine. Glucinum oxide gives the chloride $GlCl_2$ under the same conditions, but titanium yields chiefly a yellow very volatile substance, which is a titanic oxychloride. The oxides of lanthanum, cerium, europium, gadolinium, terbium, and dysprosium all give chlorides of the type MCl_3, all of which are white, with the exception of $DyCl_3$, which is light yellow. The four last named elements yield chlorides which when fused form crystalline masses. They are only very slightly volatile at their melting-points, and give colourless solutions which are but little hydrolysed. Gadolinium and dysprosium give oxychlorides when air is passed over their fused chlorides. DyOCl is yellowish green, and GdOCl forms a white amorphous-looking mass. These oxychlorides are not volatile at a red heat; they dissolve in dilute sulphuric and nitric acid after some days.

Diglycolic Acid and its Homologues.—E. Jungfleisch and M. Godchot.—Diglycolic acid can be prepared by treating a molecule of sodium ethyl glycolate in anhydrous ether with a molecule of ethyl monochloracetate:—

$$C_2H_5-CO_2-CH_2-Cl + ONa-CH_2-CO_2-C_2H_5 = NaCl + C_2H_5-CO_2-CH_2-O-CH_2-CO_2-C_2H_5.$$

The diglycolic ether is separated by fractional distillation and gives the acid on saponification. The diethyl ether of the new compound methyl diglycolic acid may be prepared by the action of sodium ethyl glycolate upon ethyl α-bromopropionate sodium ethyl lactate upon ethyl chloracetate:—

$$C_2H_5-CO_2-(CH_3)CH-Br + NaO-CH_2-CO_2-C_2H_5 = NaBr + C_2H_5-CO_2-(CH_3)CH-O-CH_2-CO_2-C_2H_5;$$

$$C_2H_5-CO_2-CH_2-Cl + NaO-CH(CH_3)-CO_2-C_2H_5 = NaCl + C_2H_5-CO_2-CH_2-O\ CH(CH_3)-CO_2-C_2H_5.$$

It is an insoluble liquid boiling at 122—125° under 20 mm. Its density at 20° is 1·0743. From it may be prepared the free acid, which is a hygroscopic substance melting at about 30°. Its alkaline and alkaline earth salts are very

soluble in water and insoluble in alcohol. When distilled *in vacuo* it gives an anhydride, $O<\begin{matrix}CH_2-CH-CO\\CH_2-CO\end{matrix}>O$, which yields a methyl diglycolic imide with ammonia. Dilactylic ether with a concentrated aqueous solution of ammonia gives dilactylic diamide, which readily loses one molecule of ammonia, giving dilactylic imide, $O<\begin{matrix}CH_3-CH-CO\\CH_3-CH-CO\end{matrix}>NH$.

Syntheses by means of Mixed Magnesium-zinc Organic Derivatives. Unsaturated $\alpha\beta$-Acyclic Ketones.—E. E. Blaise and M. Maire.—Primary or secondary acid alcohols corresponding to δ-chlor acids are readily transformed into acetic ethers, which, when treated with thionyl chloride, give the acid chlorides; these last react with the mixed magnesium-zinc organic derivatives, giving β-acetoxy-ketones, which may be saponified quantitatively to the unsaturated ketones. When the alcoholic function of the acid alcohol is tertiary it is not possible to acetylate it, but it has been found that in this case the chloride of the unsaturated acid reacts with the mixed organo-metallic substance, giving the corresponding unsaturated ketone. When a magnesium organic derivative acts on ethyl semiortho-oxalate the reaction is expressed by the equation—

$$CO_2C_2H_5-C(O-C_2H_5)_3 \rightarrow \begin{matrix}R-CH_2\\R-CH_2\end{matrix}>C-C(O-C_2H_5)_2 \rightarrow \begin{matrix}OH\\CH_2-R\end{matrix}$$

$$\begin{matrix}R-CH_2\\R-CH_2\end{matrix}>\underset{OH}{C}-CO-CH_2 \quad R \rightarrow \begin{matrix}R-CH_2\\R-CH\end{matrix}>C-CO-CH_2-R.$$

For this reaction it is necessary to employ a large excess of metallic derivative.

New Brominated Derivatives of Pyridine.—L. Barthe.—Sodium hypobromite has no action upon pyridine at temperatures below 100°, but if hydrochloric acid is added gradually to a mixture of equal volumes of pyridine and hypobromite, and the whole is heated, a golden-yellow liquid is obtained with an odour like that of nitrobenzene. When the solution is evaporated a crystalline residue is left, composed of sodium chloride and chlorate, and a brominated organic substance, which may be isolated by means of absolute alcohol, from which it separates in white crystals. The properties and analysis of these crystals show that they are pyridine bromhydrate, $C_5H_5N.HBr$. If bromine is added to the yellow liquid mentioned above, on cooling red crystals separate; they are very stable, fusing at 89—90°, and distilling without decomposition at 230° (760 mm. pressure). These crystals are tribromopyridine, $C_5H_2NBr_3$. Monobrompyridine may be prepared by adding bromine to pyridine and evaporating off the excess of the former on a water-bath. A gummy residue is thus obtained, from which may be extracted colourless crystals, by allowing it to stand with alcohol. These consist of C_5H_4NBr.

Action of γ- and δ-Brominated Ethers on Cyanacetic, Malonic, and Methyl Malonic Ethers.—G. Blanc.—When the γ-brominated ether, resulting from the action of phosphorus pentabromide and alcohol on the mixture of lactones formed by the reduction of $\alpha\alpha$-dimethyl-succinic acid, is treated with sodium ethyl cyanacetate, malonate, or methylmalonate, the ether of 2.2-dimethyl-cyclopropane carboxylic acid, $CH_3>\underset{CH-CO_2H}{\overset{CH_3}{C}}-CH_2$, is formed.

The isopropylcyclopropane carboxylic acid is made similarly, starting with isopropyl succinic acid, while the product of the condensation of dimethyl-3.3-bromovaleric acid with sodium ethyl malonate or methyl malonate is dimethyl-3.3-pentanoic acid (4.5),—

$$\begin{matrix}CH_3\\CH\end{matrix}>\underset{CH_2}{\overset{CH_3}{C}}<\begin{matrix}CH_2\\CO_2H\end{matrix}.$$

MISCELLANEOUS.

British Association for the Advancement of Science.—The following were the Officers and Committee of Section B (Chemistry) at the Leicester Meeting of the British Association:—

President—Prof. A. Smithells, B.Sc., F.R.S.

Vice-Presidents—Prof. Wyndham Dunstan, M.A., LL.D., F.R.S.; Prof. W. J. Pope, F.R.S.; Sir William Crookes, F.R.S.; Sir Henry E. Roscoe, F.R.S.

Secretaries—Prof. A. W. Crossley, D.Sc., Ph.D., F.R.S. (Recorder); E. F. Armstrong, Ph.D., D.Sc.; F. M. Perkin, Ph.D.; J. H. Hawthorn, M.A.

Committee—Prof. R. Abegg; Prof. H. E. Armstrong, F.R.S.; J. L. Baker; J. Carter Bell; Prof. Phillips Bedson; Dr. O. Boudouard; Dr. Horace T. Brown, F.R.S.; Dr. Cain; Dr. F. D. Chattaway, F.R.S.; Sir James Dewar, F.R.S.; Dr. Desch; Prof. H. B. Dixon, F.R.S.; Prof. Divers, F.R.S.; Prof. Donnan; T. Fairlie; Prof. F. Haber; A. Vernon Harcourt, F.R.S.; A. D. Hall; Prof. G. G. Henderson; H. Hilton; Dr. H. R. Le Sueur; Dr. T. M. Lowry; Dr. F. M. Jaeger; Dr. H. O. Jones, Prof. Kauffmann; Dr. A. Mackenzie; Dr. H. Marshall, F.R.S.; Prof. McLeod, F.R.S.; Prof. H. A. Miers, F.R.S.; Dr. Forster Morley; Prof. R. Nasini; Dr. R. H. Pickard; Prof. Orton; H. Ramage; Sir William Ramsay, K.C.B., F.R.S.; Prof. T. W. Richards; Prof. J. Sakurai; Prof. Tilden, F.R.S.; Prof. Senier; Dr. Ida Smedley; Prof. Soddy; Dr. J. F. Thorpe; Prof. A. Tschitschibabin; Dr. A. E. Tutton, F.R.S.; W. Marshall Watts; Prof. A. Werner.

The Papers brought before the Section were as follows:—

President's Address.

Discussion on "Valency," opened by Prof. W. J. Pope, and in which Prof. Werner (Zürich), Prof. Abegg (Breslau), Prof. Jaeger (Amsterdam), Prof. Kauffmann (Stuttgart), Prof. J. J. Thomson, Mr. W. Barlow, and others took part.

Joint Discussion with Section G (Engineering) on "Explosion Temperatures," opened by Mr. Dugald Clerk, and in which Dr. Boudouard (Paris), Prof. Haber (Karlsruhe), Prof. B. Hopkinson, Prof. H. B. Dickson, and others took part.

Prof. Phillips Bedson—Experiments illustrative of the Inflammability of Mixtures of Coal-dust and Air.

Prof. H. B. Dixon—Ignition-point of Gases.

Prof. H. E. Armstrong—Condition of Salts in Concentrated Solution.

Prof. Sir James Dewar and Dr. H. O. Jones—Carbonyl Compounds.

Dr. K. S. Caldwell—Conductivity of Electrolytes in Pyridine and other Solvents.

Dr. A. McKenzie—Application of Grignard's Reaction.

Prof. Tschitschibabin (Moscow)—Triphenylmethyl.

Prof. Jaeger—On Substances which form three different Liquid Phases.

Dr. Chattaway—Copper Mirrors.

Prof. Richards—Atomic Weights.

Dr. Boudouard—Carbon Suboxide.

Mr. A. E. Pratt—Calcium; its Properties and Possibilities.

Reports of Committees—

The Transformation of Aromatic Nitramines.

The Study of Hydroaromatic Compounds.

Preparation of a New Series of Wave-length Tables of the Spectra of the Elements.

Dynamic Isomerism.

The Study of Isomorphous Sulphonic Derivatives of Benzene.

Discussion on "The Chemistry of Wheat and Flour, with Special Reference to Strength," opened by Mr. A. E. Humphries, President of the National Association of British and Irish Millers. The following Members

took part:—Messrs. R. H. Biffen, T. B. Wood, A. D. Hall, Horace Brown, J. L. Baker, A. J. Banks, E. F. Armstrong, E. S. Watkins.

Dr. A. D. HALL—Production of Acid or Alkaline Reactions in the Soil by Artificial Manures.

Eucalyptus Oil from Queensland.—The British public owes much to Australia for the merino wool and frozen meat so extensively used here for clothing and food, respectively, and amongst the by-products imported an important one is eucalyptus oil, some of the best brands of which come from the Colony of Queensland, made from *Eucalyptus citriodora*, the lemon-scented gum. The gum-tree has many virtues, and its power in freeing districts where it grows of miasmatic influences, as in the Roman Campagna, is well known. It is only of recent years that the preparation of oils for medicinal purposes from the leaves of the gum has taken place, one of the earliest trials on a commercial scale being tried at Gladstone, a town in Queensland named after an experiment in colonisation tried by Mr. Gladstone in 1847. The industry must be worth some £50,000 a year to Australia now. Eucalyptus oil from Queensland is also used extensively for scented soaps, and for flavouring, and the industry is now being systematised and governed by the results of scientific investigation.

UNIVERSITY OF DURHAM.

ARMSTRONG COLLEGE, Newcastle-on-Tyne.

Principal—SIR ISAMBARD OWEN, D.C.L., M.D.

SESSION OF 1907-8.

MATRICULATION and EXHIBITION EXAMINATIONS, SEPTEMBER 30th to OCTOBER 5th.

OPENING of TERM, OCTOBER 8th.

Particulars of Curricula for University Degrees and College Diplomas in ENGINEERING, ELECTRICAL ENGINEERING, NAVAL ARCHITECTURE, MINING, METALLURGY, AGRICULTURE, PURE SCIENCE, and LETTERS, as well as of Fellowships, Scholarships, and Exhibitions, and of facilities for residence, on application to—

F. H. PRUEN, Secretary,
Armstrong College, Newcastle-on-Tyne.

UNIVERSITY OF BIRMINGHAM.

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UNIVERSITY of GLASGOW.

SESSION 1907-8.

[*The Classes for Women in Medicine and Arts are conducted in a separate building (Queen Margaret College), and are taught by Professors of the University and other Lecturers appointed by the University Court. For details see separate advertisement*].

The MEDICAL SESSION will be opened on THURSDAY, the 17th OCTOBER, 1907.

WINTER COURSES.

Zoology, Elementary, 9 a.m.; and Zoological Laboratory, Elementary, 11 a.m. or 3 p.m.—Professor GRAHAM KERR, M.A.

Chemistry, 10 a.m.; and Chemical Laboratory, 10 a.m. to 4 p.m.—Professor FERGUSON, M.A., LL.D., F.S.A.

Organic Chemistry, Elementary.—T. S. PATTERSON, Ph.D.

Anatomy, Junior, 11 a.m.; Senior, 1 p.m.; and Practical Anatomy, 9 a.m. to 4.45 p.m.—Professor CLELAND, M.D., LL.D., D.Sc., F.R.S., and Demonstrators.

Physiology, 12 noon; and Physiological Laboratory.—Professor NOEL PATON, B.Sc., M.D., and Assistants.

Physiological Chemistry.—E. P. CATHCART, M.D.

Materia Medica and Therapeutics, 11 a.m.; and Pharmaceutical Laboratory.—Professor STOCKMAN, M.D.

Pathology, Systematic, 3 p.m.—Professor MUIR, M.A., M.D.

Surgery, 12 noon.—Prof. Sir WILLIAM MACEWEN, M.D., LL.D., F.R.S.

Midwifery, 2 p.m.—Professor MURDOCH CAMERON, M.D.

Practice of Medicine, 11 a.m.—Prof. Sir T. M'CALL ANDERSON, M.D.

Clinical Medicine, 9 a.m.—Professor GEMMELL, M.D., and Professor Sir T. M'CALL ANDERSON, M.D.

Clinical Surgery, 9.15 a.m.—Professor Sir HECTOR C. CAMERON, M.D., and Professor Sir WILLIAM MACEWEN, M.D., LL.D., F.R.S.

Public Health, 12 noon, four days weekly; Public Health Laboratory, 10 a.m. to 4 p.m.—Professor GLAISTER, M.D., D.P.H. (Camb.).

Ear, 4 p.m., Mon. (University); Practical Instruction as may be arranged.—THOMAS BARR, M.D.

Throat and Nose, 4 p.m., Thurs. (University); Tues. or Fri. (Western Infirmary).—JAMES WALKER DOWNIE, M.B.

SUMMER COURSES.

Commencing on WEDNESDAY, 22nd APRIL, 1908.

Physics, 11 a.m.—GEORGE W. WALKER, M.A.

Practical Physics, 9 to 11 a.m., or 1 to 3 p.m.—Professor GRAY, M.A., LL.D., F.R.S.

Botany, 8 a.m.; and Botanical Laboratory, 9 a.m. to 4 p.m.—Professor BOWER, Sc.D., F.R.S.

Clinical Medicine, 9 a.m.—Professor GEMMELL, M.D., and Professor Sir T. M'CALL ANDERSON, M.D.

Clinical Surgery, 9.15 a.m.—Professor Sir HECTOR C. CAMERON, M.D., and Professor Sir WILLIAM MACEWEN, M.D., LL.D., F.R.S.

Chemical Laboratory, 10 a.m. to 4 p.m.—Professor FERGUSON, M.A., LL.D., F.S.A.

Organic Chemistry, Elementary.—T. S. PATTERSON, Ph.D.

Practical Anatomy, 9 a.m. to 4 p.m.—Professor CLELAND, M.D., LL.D., D.Sc., F.R.S., and Demonstrators.

Embryology, 11 a.m.; and Embryological Laboratory, 9 a.m. to 4 p.m.—JAMES F. GEMMILL, M.A., M.D.

Applied Anatomy, 1 p.m., Mon., Wed., Fri.—ROBERT KENNEDY, M.A., D.Sc., M.D.

Practical Pharmacy, 12 noon.—Professor STOCKMAN, M.D.

Practical Physiology, 9 to 11 a.m.; and Physiological Laboratory.—Professor NOEL PATON, B.Sc., M.D., and Assistants.

Medical Jurisprudence and Public Health, 11 a.m.; and Public Health Laboratory.—Professor GLAISTER, M.D., D.P.H. (Camb.).

Practical Pathology, 1 to 3 p.m.—Professor MUIR, M.A., M.D.

Operative Surgery, 12 noon, with practical work at other hours.—Professor Sir WILLIAM MACEWEN, M.D., LL.D., F.R.S.

Diseases of Women, 2 p.m., Tues., Thurs., Fri.—Professor MURDOCH CAMERON, M.D.

Insanity, 12 noon, Wed. (University); 10 a.m. Sat. (Gartnavel).—LANDEL R. OSWALD, M.B.

Ear, 4 p.m., Mon. (University); Practical Instruction as may be arranged.—THOMAS BARR, M.D.

Throat and Nose, 4 p.m., Thurs. (University); Tues. or Fri. (Western Infirmary).—JAMES WALKER DOWNIE, M.B.

WESTERN INFIRMARY.—This Hospital, near the University, contains over 400 Beds for Medical and Surgical Patients; also Wards for Skin Diseases, and one for Diseases peculiar to Females.

DEGREES.—FOUR Medical Degrees are conferred under the new Regulations, viz., Bachelor of Medicine (M.B.) and Bachelor of Surgery (Ch.B.), which must be taken together; Doctor of Medicine (M.D.), and Master of Surgery (Ch.M.); all of which are recognised by the Medical Acts as qualifying for Practice throughout the British dominions. The Degrees of B.Sc. and D.Sc. in Public Health, and of B.Sc. in Pharmacy, are also conferred.

FEES.—The Fee for each Systematic Class is, as a rule, £4 4s. The Fee for M.B. and Ch.B. is £23 2s.; for M.D., £10 10s.; for Ch.M., £10 10s.; for B.Sc., £6 6s.; for D.Sc., £10 10s.

BURSARIES.—Bursaries to the annual amount of upwards of £1000 are restricted to Medical Students, whilst Scholarships and Fellowships to the amount of upwards of £1600 may be held by Medical Students who have gone through the Arts Course.

Full particulars as to the Course of Education and Examination required for the Degrees, and the Preliminary Examination required to be passed by Students before beginning Medical study, will be found in the University Calendar (by post 3s. 4d.); or a Syllabus of the Regulations, Fees &c., may be obtained by applying to Mr. W. INNES ADDISON, Assistant Clerk.

THE CHEMICAL NEWS.

Vol. XCVI., No. 2490.

FIRST DECAY PRODUCTS OF ACTINIUM (EMANIUM).

A New Emanation, and the Formation of Helium from Actinium.

By F. GIESEL.

I. *Radio-actinium.*

In earlier articles (*Berichte*, 1904, xxxvii., 1697; 1905, xxxviii., 778) I have already stated that the artificial barium sulphate precipitates obtained from emanium solutions retain their activity for many months. Also, I noticed that the strontium sulphate separated from emanium preparations decays equally slowly (*Berichte*, 1904, xxxvii., 3966). Hence, it must be assumed that the chief constituent of these sulphuric acid precipitates is not actinium X with a half decay period of ten days, but a substance with a longer duration of life.

Recent determinations of the times of decay (period of decay to the half value nineteen days) agree very well with radio-actinium, which was, meanwhile, discovered by Hahn (period of decay to the half value nineteen and a-half days) (*Berichte*, 1906, xxxix., 1605).

From my earlier articles mentioned above, it now appeared that sulphuric acid is capable of precipitating radio-actinium, at least if strontium or barium is present. It has also already been stated (*Berichte*, 1904, xxxvii., 3965) that the insoluble sulphate can be converted into soluble chloride, and the active substance (*i.e.*, the radio-actinium) again quantitatively precipitated as carbonate (*Berichte*, 1904, xxxvii., 3965). Ammonia, on the contrary, does not precipitate it, or the radio-actinium can be carried down on precipitating the hydroxides only in presence of certain salts, *e.g.*, thorium or iron salts. Hence, probably radio actinium belongs to the alkaline earths, or is closely allied to them. Spectrograms of the spark light of strong preparations obtained from the chloride, however, always gave only strontium as the chief constituent besides very little calcium and barium. No new lines could be detected.

Hahn used finely divided sulphur, which had been separated from sodium thiosulphate, to precipitate the radio-actinium. Similarly, I have often observed that sulphur, which separates when sulphuretted hydrogen is led into cerium or iron salts, produces the same effect. But possibly in both reactions it is not the mechanical action of the sulphur which is the cause of this, as has been assumed, but the formation of some sulphuric acid, which then undoubtedly effects the precipitation of the radio-actinium. (Sodium thiosulphate itself mostly contains some sulphate). The same holds good for the method used by Debierne and Marckwald to separate thorium (or radio-actinium) by sodium thiosulphate, when it is known that the thiosulphate is decomposed. Marckwald has already stated (*Berichte*, 1905, xxxviii., 2264) that in this method all the actinium remains in the solution, and that the thorium again slowly loses its activity. I have several times convinced myself of the correctness of Marckwald's statements. Debierne says that actinium is allied to thorium, but this must now be corrected. Actinium is never precipitated with thorium from a mixture of the rare earths of pitchblende, but always remains with the cerium earths, especially with lanthanum, as I have found.

I must mention that I did not get my strong radio-actinium preparations free from β-radiation, and they contained some emanation, which is easily explained, for after a short time the further decay products must result. Hahn also states that the α-radiation of radio-actinium is approximately pure only a short time after its preparation.

II. *Actinium* X.

As may be inferred from what has been said above, actinium X remains practically unprecipitated by sulphuric acid. It can easily be separated from actinium by ammonia, by the well known method. But the solubility in ammonia is limited, so that the actinium X, after sufficient concentration is partially precipitated by ammonia (*cf. Berichte*, 1905, xxxviii., 778); also by alkali carbonates, in this case with traces of strontium. In the filtrate a considerable amount of actinium X still remains. All three partial separation methods applied in succession gave, on an approximate determination based on only three observations, a half constant of eight or nine days.

My statements in the *Berichte* (1905, xxxviii., 777), that actinium X is precipitated by sulphuric acid, thus require modification now that radio-actinium is known. This latter is first precipitated, and then actinium X results from it.

Sulphuric acid can be used to separate radio-actinium and actinium X.

III. *New Emanation.*

In order to test Boltwood's statement, that "actinium slowly forms radium," 0·2 grm. of a very strong emanium preparation from radium mother-liquor (*Berichte*, 1903, xxxvi., 343), which was four years old, was dissolved in hydrochloric acid, and some sulphuric acid was added after filtration. If radium had been formed, it must have been found in the precipitate which resulted. Unfortunately, this precipitate was so small that a spectrographic examination was impossible. The activity of the small filter with the substance was, however, so great that only a very small fraction of it could be used to determine the change of activity with time, and an electroscope with a very high capacity was employed. But the activity did not increase as is the case with radium, but decreased at the rate which is characteristic for radio-actinium, as was to be expected. However, small amounts of radium could not have been detected thus.

As, in consequence of the great differences in the rates of decay of radium and actinium emanations (period of decay to the half value for radium emanation four days, for actinium emanation four seconds), it is easy to detect traces of the former in the latter, the emanation of the little filter was collected during a period of some days; it was led into a test-tube closed with wadding and connected with a glass flask of about a quarter of a litre capacity. If an emanation with a longer duration of life, such as actinium emanation, were formed, it would diffuse into the glass flask. After about half-an-hour after separating the tube with the filter, the gaseous contents of the flask were introduced by displacement with water into Elster and Geitel's leakage apparatus previously partially exhausted, putting in between a securely closed wadding filter. In all experiments which were repeatedly carried out with different preparations and even with a matured actinium preparation itself, the electroscope showed the presence of an emanation by a loss of charge of 200 to 400 volts in an hour, according to the quantity and the time the radio-active substance was left in the collecting apparatus. But the emanation could not be radium emanation, for the characteristic rise of leakage value did not occur during the first one or two hours, nor the following decrease. On the contrary, a much slower increase occurred, reaching about double the original value in the first two or three days (500 to 700 volts per hour). Then the activity remained constant at this value during a time of observation of from two to three weeks. After exposing the apparatus to the air in a few hours the leakage value had sunk almost to the normal, and on the next day it reached the normal. Hence, no solid active substance (induced activity) can have been precipitated on the interior of the apparatus. No substance in the form of

dust could be present because wadding filters were used. More probably a gaseous substance, possessing an exceedingly long life, was present.

The new emanation seems to proceed from the decay of actinium emanation in minute quantities, unless an unknown substance, which in its turn gives the new emanation, is contained in the radio-actinium or emanium preparation.

IV. *Formation of Helium from Actinium.*

Almost at the same time as I prepared my radium-helium tubes (*Berichte*, 1905, xxxviii., 2299), *i.e.*, more than two years ago, I enclosed similarly 0·5 grm. of a relatively strong emanium preparation in the form of oxide in a Geissler tube, and exhausted as far as possible. The vacuum was maintained unaltered during this time, and helium could not be detected when the gas was faintly luminous. But latterly it has been possible, after heating the substance, to identify in the spectrum of the gas the D_3 line of helium. This agrees with an earlier statement of Debierne (*Comptes Rendus*, 1905, cxli., 383), who found helium in the gases developed from actinium, just as Ramsay detected it in the gases obtained from radium. —*Berichte*, 1907, xl., 3011.

THE RADIATION OF THORIUM PRODUCTS.

By OTTO HAHN.

In a recent communication on "A New Intermediate Product from Thorium (*Berichte*, 1907, xl., 1462) I reported briefly on experiments which showed that thorium does not decay directly to radio-thorium, and that probably another product exists between these two, which unlike radio-thorium emits no α-rays, but is superior to the latter in its duration of life. I gave about two years as the decay constant of radio-thorium (see Note), and estimated that the constant for this new element was seven years. (The value seven years was evidently too high).

(Note.—Shortly before my communication an article by G. A. Blanc appeared in *Lincei Rend.*, 1907, xvi., 261) on "The Decay Constant of Radio-thorium"; he found the value 737 days. Unfortunately, when I wanted to refer to this article I could not get access to it).

Further experiments have now completely confirmed the existence of this intermediate product, so that in the future I shall allude to it by the name mesothorium. In the article quoted I stated that in the technical preparation of thorium nitrate the mesothorium was separated from the thorium, but not the radio-thorium. Then there followed a decrease of the activity because the radio-thorium decayed. After some years the lowest stage was reached, and then the activity again slowly increased, as with the reformed mesothorium some new radio-thorium also resulted.

When exact measurements were taken of these processes different results were obtained for the activity according as the α-radiation, the emanation, or the β-rays were compared.

Hence, it must be concluded that besides radio-thorium and its derivatives the first members of the thorium series also emit rays, and this conclusion can be confirmed partly by an indirect and partly by a direct method.

As regards the α-rays it was formerly assumed that there were four different sorts in the thorium products. Before the separation of the radio-thorium these were distributed among thorium, thorium X, the emanation, and thorium B. Then I showed that radio-thorium emits α-rays, and hence inferred that thorium itself sends out no rays; for the 25 per cent α-activity, which Rutherford and Soddy investigated, and which is inseparable from thorium, is obviously due to the radio-thorium.

The communications on the subject of inactive thorium which have been published by various investigators can be satisfactorily explained if it is assumed that in the products examined, if they really were thorium, by some means the radio-thorium had been separated.

I then found a fifth α-radiation product in the active precipitate of thorium, for it appeared that the substance known as thorium B has a complex nature, and emits two sorts of α-rays. The carriers of these rays were called thorium B and thorium C.

I have now come to the conclusion that a sixth sort of α-rays exists, thorium itself, and not only the radio-thorium emitting α-particles.

Although the proof of this was arrived at indirectly, nevertheless three different methods led to the same result.

The methods used were:—

1. Comparison of the activities of thorium preparations of different ages by the effect of the α-rays and of the emanation.

The differences in the effect of the emanation are greater than those of the α-rays, as the activity of thorium itself is added as a constant quantity to the measurements of the α-rays, but not to those of the emanation.

2. Preparation of thorium preparations of different age from thorium X.

The inseparable α-activity is composed of two quantities, the constant activity of the true thorium and the activity of the radio-thorium. If the latter is present with its decay products in excess, as is the case with new thorium preparations, a larger fraction of the total quantity is removed in the separation of the thorium X than in old preparations, in which less radio-thorium + thorium X is present.

3. Preparation of radio-thorium free from thorium X.

The inseparable α-activity is smaller than in any ordinary thorium preparation, as the activity of the true thorium is removed.

The existence of a typical α-radiation of true thorium seems thus proved, and the question of the so-called active thorium appears to be finally settled.

It has hitherto been assumed that the β-radiation of thorium arises only from the active deposit. Exact experiments on the origin of the β-rays were described by Levin (*Phys. Zeit.*, vii., 513). He was able to reduce the β-activity of thorium to a small percentage of its original value by separating the thorium X from the thorium or radio-thorium. Levin therefore came to the conclusion that neither thorium nor radio-thorium emits penetrating β-rays, and that such β-rays are only sent out by the last products, thorium B or C.

Recently, v. Lerch (*Phys. Zeit.*, vii., 913) has shown that thorium A also emits a kind of β-radiation, which, however, cannot be compared as regards penetrative power with that of thorium B + C. The rays are scarcely more penetrating than α-rays, and probably they are a sort of specially slow β-rays, or so-called δ-rays.

In my experiments with thorium preparations of different ages I obtained the singular result that the β-radiation of the old preparations did not differ from that of the new by the amount that was to be expected. Thus, as the thorium B and C is always proportional to the amount of emanation—under the same conditions—the fluctuations in the β-activity must follow those of the emanation effect provided that thorium B + C is the only cause of the β-rays in thorium. As the experiments did not confirm this there must be another source of β-rays in old thorium preparations.

The next thing to be done was to search for the cause of such β-radiation in the newly discovered mesothorium, and it was found that mesothorium emits β-rays. (It must be assumed that mesothorium also emits γ-rays, but this has not yet been investigated). The experiments of Levin quoted above were not affected by this, for his thorium preparations evidently did not contain mesothorium, for they were not old enough. Moreover, this small quantity was not sufficient for measurement, which, of course, was not recognised as mesothorium was not then known.

It could also be proved directly that mesothorium emits β-rays. I succeeded in separating mesothorium from old thorium preparations, which showed itself by the continual increase of activity and power of emanation. The preparations thus obtained show a β effect which is much

greater than that of equally strong radio-thorium or ordinary thorium preparations under the same conditions of emanation. I have recently obtained a preparation which emits about one hundred times more β-rays than would correspond to its α-activity. Hence, it appears that the specimen will increase considerably in α effect until the newly formed radio-thorium is in radio-active equilibrium with the mesothorium.

I hope shortly to be able to give a full statement of the numerical results elsewhere, and will here append only a list of the different thorium products with the rays they emit in order of formation.

Thorium	α rays
Mesothorium	β ,,
Radio thorium	α ,,
Thorium X	α ,,
Emanation	α ,,
Thorium A	slow β ,,
Thorium B + Thorium C	α, $\beta+\gamma$,,

—*Berichte*, 1907, xl., 3304.

IRON CARBONYLS.*

By Sir JAMES DEWAR, M.A., D.Sc., F.R.S., and H. O JONES, M.A., D.Sc.

Iron pentacarbonyl, $Fe(CO)_5$, is a yellow liquid which resembles nickel tetracarbonyl in its chemical and physical properties, but it is more stable towards chemical reagents. When decomposed by reagents it always gives rise to *ferrous* salts.

The most striking difference observed between its behaviour and that of nickel carbonyl is due to the action of light, iron pentacarbonyl being decomposed with evolution of carbon monoxide and formation of an orange crystalline solid, *diferro-nonacarbonyl*, $Fe_2(CO)_9$. This change is supposed to take place in two stages, represented by $Fe(CO)_5 = Fe(CO)_4 + CO$ and $Fe(CO)_4 + Fe(CO)_5 = Fe_2(CO)_9$, since when iron pentacarbonyl is dissolved in nickel carbonyl it is not affected by light, due, it is suggested, to the formation of an unstable compound, $FeNi(CO)_9$.

The decomposition induced by light is reversed slowly in the dark. Above 56° C. light has no action on iron pentacarbonyl; this is explained by supposing that the direct action induced by light is a change that is almost unaffected by temperature, like the reaction between ferric chloride and oxalic acid and some other photochemical actions, whereas the reverse action of carbon monoxide and the diferro-nonacarbonyl has a normal temperature coefficient.

When diferro-nonacarbonyl is heated alone a dark green liquid is produced; this consists chiefly of iron pentacarbonyl; on continued heating the green colour disappears, and iron is deposited; the change is then represented by the equation $2Fe_2(CO)_9 = 3Fe(CO)_5 + Fe + CO$.

When substances like hydrocarbons or ether are present in excess and the temperature is not allowed to exceed 100° C. an intensely green-coloured solution is obtained; no solid is deposited, and no gas is evolved. The dark green solution under suitable conditions deposits dark green lustrous crystals which represent a third compound of iron and carbon monoxide, *iron tetracarbonyl*, $Fe(CO)_4$, which has a high molecular weight. When alcohol or pyridine is used as solvent in which to heat the diferro-nonacarbonyl the solution obtained is red, and no solid could be obtained from these solutions.

Iron tetracarbonyl is very stable towards reagents; it dissolves in most organic solvents to give dark green solutions which exhibit a characteristic absorption band in the yellow. In pyridine and alcohol, however, the colour of the solution is green at first, but changes slowly on standing and quickly on warming to a deep red; the red solutions show no selective absorption.

Both diferro-nonacarbonyl and iron tetracarbonyl when decomposed by reagents such as concentrated sulphuric acid give carbon monoxide and *ferrous* salts.

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

ON THE CONDUCTIVITY OF ELECTROLYTES IN PYRIDINE AND OTHER SOLVENTS.*

By KENNETH SOMERVILLE CALDWELL.

I. *Comparison of Acids and Pseudo-acids in Pyridine.*

Although previous experimenters have compared acids and pseudo-acids as regards their conductivities in solvents which form hydrogen ions (*e.g.*, alcohols and mixtures of alcohols and water) (Hantzsch and Voegelen, *Ber.*, xxxv., 1001), no investigations have been carried out in solvents which are of such a nature that the acid is dissolved either entirely or partly in the form of a salt. Liquid ammonia would at once suggest itself as a suitable medium, more especially as a number of widely differing compounds have already been examined in this solvent (Franklin and Kraus, *Am. Chem. Journ.*, xxiii., 277; xxvii., 196), but owing to the obvious experimental difficulties it was not employed. The attempt to substitute the saturated amine piperidine instead of ammonia yielded results of little interest, owing to the extremely small conductivity of solutions in this solvent. The unsaturated amine pyridine, on the other hand, proved to be more suitable.

Members of the following classes of compounds were examined:—

A. Acids which exist in one form only.
   1. The strong mineral acids and sulphonic acids.
   2. Organic acids.

B. Acids which exist in isomeric forms—pseudo-acids.
   1. Nitro-compounds—(*a*) nitrohydrocarbons; (*b*) nitrophenols; (*c*) nitramines.
   2. Oximido-compounds—(*a*) oximido-carboxylic esters; (*b*) oximido-ketones and quinonoximes; (*c*) nitrolic acids.
   3. Compounds containing the group —CO.NH—.
   4. Related nitrogen compounds, *e.g.*, aminotetrazol, phenyloxytriazol carboxylicester.
   5. Ketonic-enolic compounds.
   6. Oxyazobenzenes.

The pyridonium halides in pyridine exhibit the same differences in conducting power that is noticed in solutions of their alkali salts in pyridine (Laszynski and Gorski, *Zeit. fur Elektrochem.*, iv., 290), methyl alcohol (Carrara, *Jahrb. fur Elektrochem.*, iii., 12), and liquid sulphur dioxide (Walden and Centnerszwer, *Zeit. für Elektrochem.*, xi., 219); only in pyridene the difference is much more marked (*e.g.*, HCl. $\mu_{32} = 1{\cdot}16$, HBr. $\mu_{32} = 7{\cdot}12$, HI. $\mu_{32} = 27{\cdot}4$). With this exception, the "true" acids compared among themselves follow approximately the same order in pyridine as in water; a fact which also applies to the pseudo-acids. The stronger the tendency to pass into an isomeric form, *i.e.*, the more completely the pseudo-acid form is isomerised and ionised in aqueous solution, the better does its pyridine solution conduct. There is to a certain extent a parallel between the affinity constants in aqueous solution and the conductivities in pyridine. When, however, the true acids are compared with the pseudo-acids, it is noticed that in pyridine the latter yield very much better conducting solutions than do "true" acids, having approximately the same, or even very much greater, affinity con-

* Report of work carried out in Leipzig under the direction of Professor A. Hantzsch. Read before the British Association (Section B), Leicester Meeting, 1907.

stants. We may conclude that *when a hydrogen compound yields a pyridine solution of far better conducting power than is given by a true acid which in aqueous solution is dissociated to approximately the same extent as the hydrogen compound, the latter is a pseudo-acid.* Hexanitrodiphenylamine, for example, must be regarded as a pseudo-acid; for although, owing to its insolubility in water, its affinity constant has not been determined, the conductivity of its pyridine solution is far greater than that of all true acids, even the strongest mineral acids.

II. *On the Influence of Temperature on the Conductivity of Electrolytes.*

1. The influence of temperature on the conductivity of electrolytes may be expressed by the general equation—

$$\frac{d\mu}{dt} = c\left(i \cdot \frac{dv}{dt} + v \cdot \frac{di}{dt}\right);$$

where i = concentration of the ions, v = mean rate of migration of positive and negative ions, t = temperature, and c = constant.

If the effect of change of temperature on the rate of migration is the reverse of that on the degree of dissociation, a maximum in the temperature-conductivity curve is to be expected.

2. It may be deduced that, for a given electrolyte, the smaller the dielectric constant of the solvent the lower must lie the temperature of maximum conductivity.

3. These deductions are confirmed by the results of previous experiments on solutions in water (Noyes and Coolidge, *Zeit. Phys. Chem.*, xlvi., 323), methyl and ethyl alcohols (Kraus, *Phys. Review*, xviii., 40), ammonia (*Am. Chem. Journ.*, xxiv., 83), and sulphur dioxide (Walden and Centnerszwer, *Zeit. Phys. Chem.*, xxxix., 513), and especially by the results of the present investigation on solutions in pyridine. The influence of temperature on the electric conductivity of solutions in pyridine has been determined for a number of acids and pseudo-acids as well as for silver nitrate. The temperature of maximum conductivity is well marked, and the curves have been followed up to and beyond this point.

4. The curves are represented closely by the parabolic equations $\mu_t = \mu_0(1 + bt + ct^2)$, and the theoretically deduced expression $a = \frac{\mu_t - \mu_\tau}{\mu_\tau(t-\tau)^2}$ is taken as a measure of the temperature effect.

5. The observation of Walden and Centnerszwer, that for solutions in liquid sulphur dioxide the temperature of maximum conductivity is higher the greater the conductivity, has not been confirmed for solutions in pyridine.

6. The comparatively rapid decrease in the degree of dissociation with increase in temperature may partly explain the fact that numerous substances which at ordinary temperatures yield good conducting pyridine solutions appear, according to boiling-point determinations, to be undissociated.

III. *Abnormally High Values of Ionic Conductivity* (*cf.* Danneel, *Zeit. Elektrochem.*, xi., 249).

Solutions of salts which contain either the same cation or the same anion as the solvent itself (pyridonium salts in pyridine, formates in formic acid, acetates in acetic acid, and probably bromides in hydrobromic acid, and sulphates in sulphuric acid) show in these solvents an abnormally high conductivity in comparison with all other salts. Since all salts are dissociated to approximately the same extent, the abnormally high values of the conductivity of the first-class can only be explained by assuming an abnormally high value for the rate of migration of those ions which the salt has in common with the solvent.

This abnormal value of the rate of migration is, however, only an apparent one. The ions of such salts react with the solvent with exchange of a labile hydrogen atom.

AN AUTOMATIC VACUUM REGULATOR.

By A. E. ANDREWS.

In employing a vacuum pump in order to conduct an operation at reduced pressure, difficulties often arise owing to fluctuations in the degree of exhaustion obtained. This is especially the case when distilling under reduced pressure, for it often happens that the liquid either boils too violently or not at all. I found that this difficulty could be obviated by employing an apparatus constructed as shown in Fig. 1. It works automatically, and after adjustment maintains any desired pressure constant within very narrow limits.

The apparatus consists of a glass tube furnished with a side-arm (B), and having at its lower end a small aperture (A) closed by a hemispherical piece of indiarubber held in a short glass tube (V) perforated at the side and open at the top. This valve is pressed down by a spring (S), which is

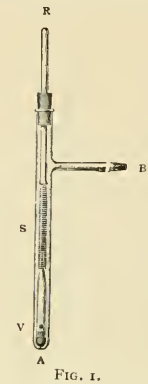


Fig. 1.

Fig. 2.

kept in position by an adjustable rod (R). The side-arm B is connected with the apparatus undergoing exhaustion. The valve is kept closed by the combined pressure of the spring and of the air in the apparatus. As the air is pumped out the pressure on the valve diminishes, until a point is reached when the external pressure is able to lift the valve, and the air thus admitted keeps the internal pressure constant. If the pressure as shown by the pump-gauge is greater than that desired, the rod R is pressed down, thus increasing the pressure of the spring, and the valve will only open when a higher degree of exhaustion is reached. By moving the rod R up or down the desired pressure may readily be obtained.

The apparatus has been constructed by Messrs. John J. Griffin and Sons, Ltd., who also make it in a form entirely of metal, in which case the sliding rod R is replaced by a screw-down rod, as shown in Fig. 2. The metal regulator seems likely to prove applicable to manufacturing plant, such as vacuum pans.

British Association for the Advancement of Science.—Mr. Francis Darwin, F.R.S., has been elected President of the Association for the year 1908-09. The meeting will be held in Dublin, from September 2nd to 9th, 1908.

Lawes Agricultural Trust.—The following gentlemen have recently been appointed on the Staff of the Rothamsted Experimental Station:—Dr. E. J. Russell, lately of the South-Eastern Agricultural College, Wye, as the Goldsmiths' Company's Assistant for the Investigation of Soils, and Dr. B. B. Hutchinson, of the Midland Agricultural and Dairy College, Kingston, Derby, as Bacteriologist.

NOTE ON THE INTERACTION OF ETHYL BROMIDE AND SILVER CHROMATE.

By ARTHUR JAQUES, B.Sc.

In presence of water, ethyl bromide and silver chromate (prepared by precipitating silver nitrate with potassium chromate—O. Mayer, *Berichte*, xxxvi., 1740) interact, yielding a red solution containing alcohol, chromium trioxide, &c., while the silver chromate is replaced by white silver bromide.

In absence of water, the reaction is slow. The two substances were placed together in a stoppered tube. In three weeks, white specks of silver bromide could be seen, and a reddish brown powder which easily went into suspension in the liquid had appeared. The volume of ethyl bromide had diminished.

The solids were filtered off, the ethyl bromide was allowed to evaporate, and aqueous potassium cyanide was poured through the filter in order to remove silver salts. The remaining solid was dried in the desiccator, but was found to be slightly changed in colour.

When heated it decomposed with evolution of light and heat, yielding chromic oxide, carbon dioxide, water, and other vapours. On treatment with aqueous caustic soda, it gave a yellow solution containing alcohol and sodium chromate. These bodies were identified by means of the iodoform reaction and precipitation with barium acetate in acetic acid solution respectively. Thus the substance is probably ethyl chromate.

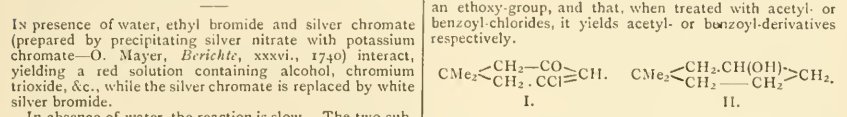
The residue obtained on heating the body always contained a small quantity of silver. Prolonged washing with potassium cyanide caused decomposition. Thus the body has never been obtained in a state of purity.

Attempts were made to wash the body with alcoholic lithium cyanide, but most of it went into the solution, from which, however, a reddish powder afterwards separated. At this point the work was suspended (1905), and it has not yet been resumed. It is hoped to obtain the substance by this method in a condition suitable for analysis at some future time.

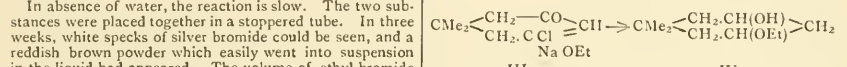
THE

STUDY OF HYDRO-AROMATIC SUBSTANCES.*

1. *The Action of Reducing Agents on* 5-*Chloro*-3-*keto*-1 : 1-*dimethyl*-Δ^4-*tetrahydrobenzene* (Crossley and Renouf, *Journ. Chem. Soc.*, 1907, xci., 63).—Some little time since (*J. Chem. Soc.*, 1905, lxxxvii., 1487), it was shown that the principal product obtained by the action of sodium in moist ethereal solution on chloroketodimethyltetrahydrobenzene (I.) was 3-hydroxy-1 : 1-dimethylhexahydrobenzene (II.), which may be described as the limit-reduction product of the chloroketone. A further study of the reaction has proved that the addition of a small quantity of alcohol to the ether has a beneficial effect, considerably increasing the yield of hydroxydimethylhexahydrobenzene, and rendering it much easier to remove the chlorine completely from the chloroketone. As alcohol had such a decided influence, it was thought advisable to try the reduction with sodium in absolute alcoholic solution. The reaction proceeded, however, in an unexpected direction, and demonstrated the fact that the chlorine atom in chloroketodimethyltetrahydrobenzene is very reactive—a fact which greatly enhances the possibilities of the use of this and similar chloroketones for synthetical purposes. Small quantities of hydroxydimethylhexahydrobenzene (II.), but principally 3-*hydroxy*-5-*ethoxy*-1 : 1-*dimethylhexahydrobenzene* (IV.) were obtained, and it is evident that the sodium ethoxide formed in the first stages of the reduction reacts with the chlorine atom of the chloroketone to give the substance represented by Formula III., which is then further reduced to the corresponding saturated compound. The constitution of the latter is proved by analysis and by the facts that a Zeisel determination shows it to contain an ethoxy-group, and that, when treated with acetyl- or benzoyl-chlorides, it yields acetyl- or benzoyl-derivatives respectively.



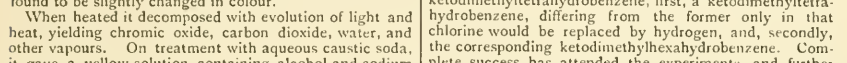
I. II.



III. IV.

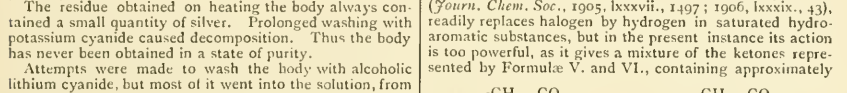
The main object of the investigation was, however, to find reducing agents, less powerful than sodium in moist ethereal solution, which would be discriminating in their action; so that it might be possible to prepare from chloroketodimethyltetrahydrobenzene, first, a ketodimethyltetrahydrobenzene, differing from the former only in that chlorine would be replaced by hydrogen, and, secondly, the corresponding ketodimethylhexahydrobenzene. Complete success has attended the experiments, and further work is in progress with the object of proving that the reactions are general ones.

The next reducing agent employed was zinc-dust in aqueous alcoholic solution, which, as previously shown (*Journ. Chem. Soc.*, 1905, lxxxvii., 1497; 1906, lxxxix., 43), readily replaces halogen by hydrogen in saturated hydroaromatic substances, but in the present instance its action is too powerful, as it gives a mixture of the ketones represented by Formulæ V. and VI., containing approximately

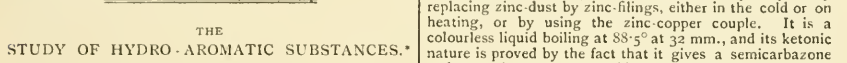


V. VI.

30 per cent of the latter. However, 3-*keto*-1 : 1-*dimethyl*-Δ^4-*tetrahydrobenzene* (V.) may be obtained quite pure by replacing zinc-dust by zinc-filings, either in the cold or on heating, or by using the zinc-copper couple. It is a colourless liquid boiling at 88·5° at 32 mm., and its ketonic nature is proved by the fact that it gives a semicarbazone and an oxime. When oxidised with potassium permanganate in the cold it yields *as*-dimethylsuccinic acid and the lactone of α-hydroxy-$\beta\beta$-dimethylglutaric acid :—



3-*Keto*-1 : 1-*dimethylhexahydrobenzene* (VI.) may be produced from chloroketodimethyltetrahydrobenzene by heating it with zinc-dust in glacial or dilute acetic acid solution. It is a colourless liquid boiling about 10° lower (75·5° at 25 mm.) than the corresponding unsaturated ketone. It forms an oxime and a semicarbazone, and when oxidised with potassium permanganate gives only $\beta\beta$-dimethyladipic acid (VII.)—a fact which proves its constitution beyond doubt.



VII.

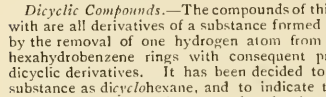
Other reducing agents investigated were zinc dust in strongly alkaline solution, also zinc-dust and hydrogen chloride in alcoholic solution. In the former case the hydrolytic action of the potassium hydroxide overshadows the reducing action of the zinc, with the result that the only product isolated was dimethyldihydroresorcin (VIII.). In the latter case a mixture of ketodimethyltetrahydrobenzene and ketodimethylhexahydrobenzene was obtained,

* Report of the Committee, consisting of Dr. E. Divers (Chairman), Prof. A. W. Crossley (Secretary), Prof. W. H. Perkin, Dr. M. O. Forster, and Dr. H. R. Le Sueur.

together with dimethyldihydroresorcin and its ethyl ether (IX.) (*Journ. Chem. Soc.*, 1899, lxxv., 775). Here, again, hydrolysis must first take place, giving rise to dimethyldihydroresorcin, which is then esterified by the alcoholic hydrogen chloride.

$CMe_2<^{CH_2---CO}_{CH_2.C(OH)}>CH.$ VIII. $CMe_2<^{CH_2---CO}_{CH_2.C(OEt)}>CH.$ IX.

Dicyclic Compounds.—The compounds of this nature met with are all derivatives of a substance formed theoretically by the removal of one hydrogen atom from each of two hexahydrobenzene rings with consequent production of dicyclic derivatives. It has been decided to refer to this substance as dic*yclo*hexane, and to indicate the positions of the various substituting groups by adopting the following scheme of numbering :—



When zinc-dust acts on chloroketodimethyltetrahydrobenzene in aqueous solution there is obtained a mixture of ketodimethyltetrahydrobenzene and ketodimethylhexahydrobenzene (V. and VI.), in which the former largely predominates. If this mixture of ketones is again treated several times with zinc-dust, it is possible to isolate pure ketodimethylhexahydrobenzene and a semi-solid mass from which a crystalline product has been separated, melting at 148°. It has the composition $C_{16}H_{26}O_2$, is believed to be 1 : 1′-*dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyl*-$\Delta^{2:2'}$-*dicyclohexene* (X.), and owes its origin to pinacone formation. Moreover, its behaviour is quite in accord with that of a substance having Formula X., for it does not give a colour reaction with concentrated sulphuric acid, nor can it be acetylated or benzoylated under the conditions employed. Further, its unsaturated nature is proved by the facts that it readily absorbs bromine, and when treated with sodium in moist ethereal solution it absorbs four atoms of hydrogen to give 1 : 1′-*dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyldicyclohexane* (XI.). Here again this saturated pinacone does not give a colour reaction with concentrated sulphuric acid, but it is surprising to find that it is acetylated or benzoylated very readily, though no explanation of this fact can be offered on the present occasion.

$CH_2<^{CMe_2.CH_2}_{CH---CH}>C(OH).C(OH)<^{CH_2.CMe_2}_{CH---CH}>CH_2.$ X.

$CH_2<^{CMe_2.CH_2}_{CH_2---CH_2}>C(OH).C(OH)<^{CH_2.CMe_2}_{CH_2---CH_2}>CH_2.$ XI.

In the preparation of hydroxydimethylhexahydrobenzene considerable difficulty was experienced at one time in obtaining the product free from halogen, and on examining the resinous by-product formed under these conditions two solid substances were separated from it, melting respectively at 178° and 173—174°. The former of these has the composition $C_{16}H_{22}O_2$, and is apparently 3 : 3′-*diketo*-5 : 5 : 5′ : 5′-*tetramethyl*-Δ-1 : 1′-*dicyclohexene* (XII.), formed by the direct coupling of two molecules of chloroketodimethyltetrahydrobenzene by the sodium. It is highly coloured (yellow), gives a brick-red disemicarbazone, thus proving its diketonic nature, and is unsaturated as shown by its ready absorption of bromine. It could not be detected in the resin formed when alcohol was added to the ether used in the reduction of chloroketodimethyltetrahydrobenzene, but much larger quantities of the second substance melting at 173—174°, and also another compound melting sharply at 212° were isolated. The latter proved to be identical with 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldic*yclo*hexane (XI.).

$CH_2<^{CMe_2.CH_2}_{CO---CH}>C\overset{Cl\ Na}{\cdots}C<^{CH_2.CMe_2}_{CH---CO}>CH_2 \rightarrow$

$\rightarrow CH_2<^{CMe_2.CH_2}_{CO---CH}>C.C<^{CH_2.CMe_2}_{CH---CO}>CH_2.$ XII.

For a long time the substance melting at 173—174° was thought to be homogeneous, as it gave on analysis numbers agreeing with the formula $C_{16}H_{30}O_2$, nor was its melting-point altered by many re-crystallisations, and, moreover, it sublimed in needles which melted at 171—172°. Nevertheless, it was found to be a mixture, for on acetylation it gave two diacetyl derivatives melting at 130° and 68°, and on benzoylation two dibenzoyl derivatives melting at 199° and 134°. The former of the diacetyl and dibenzoyl compounds (m. p. 130° and 199°) proved to be diacetyl- and dibenzoyl 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane, which substance they yielded on hydrolysis.

The above mentioned derivatives melting at 68° and 134° were separately hydrolysed with alcoholic potassium hydroxide, when they each gave a substance, $C_{16}H_{30}O_2$, melting at 183°, which is believed to be 3 : 3-*dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyldicyclohexane* (XIII.). It is readily acetylated and benzoylated, and, unlike the unsaturated or saturated pinacones, gives a decided colour reaction with sulphuric acid. Its formation would be due to the further reduction of diketotetramethyldic*yclo*hexene (XII.), although, unfortunately, sufficient of the latter material could not be isolated to try the action of reducing agents upon it.

$CH_2<^{CMe_2---CH_2}_{CH(OH).CH_2}>CH.CH<^{CH_2---CMe_2}_{CH_2.CH(OH)}>CH_2.$ XIII.

The substance melting at 173—174° is therefore a mixture of 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldic*yclo*hexane (XI.) and 3 : 3′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldic*yclo*hexane (XIII.), and it would appear therefore that in the reduction of chloroketodimethyltetrahydrobenzene with sodium in moist ethereal solution dicyclic compounds are formed both by the process of pinacone formation and by the coupling reaction of the sodium.

2. *Action of Alcoholic Potassium Hydroxide on* 3-*Bromo*-1 : 1-*Dimethylhexahydrobenzene* (Crossley and Renouf, *Journ. Chem. Soc.*, 1906, lxxxix., 1556).—The preparation of 3-bromo-1 : 1-dimethylhexahydrobenzene (XIV.) has been previously described (*Ibid.*, 1905, lxxxvii., 1497), and also the action of alcoholic potassium hydroxide on this substance (*Ibid.*, p. 1499), which was stated to give rise to 1 : 1-dimethyl-Δ^3-tetrahydrobenzene (XV.) only,

$CMe_2<^{CH_2.CHBr}_{CH_2---CH_2}>CH_2.$ XIV. $CMe_2<^{CH_2---CH}_{CH_2.CH_2}>CH.$ XV.

and not to the isomeric tetrahydrobenzene with the double bond in the Δ^2-position. This conclusion, which was based on the result of oxidation experiments, was so unexpected that it appeared desirable further to investigate the supposed 1 : 1-dimethyl-Δ^3-tetrahydrobenzene, especially as there appeared to be a fairly easy means of deciding the point at issue. If this hydrocarbon has the constitution represented by Formula XV., then on treatment with bromine it would give rise to 3 : 4-dibromo-1 : 1-dimethylhexahydrobenzene (XVI.), which, on treatment with a

$CMe_2<^{CH_2.CHBr}_{CH_2---CH_2}>CHBr \rightarrow CMe_2<^{CH=CH}_{CH_2.CH}>CH.$ XVI. XVII.

reagent capable of removing the elements of hydrogen bromide, should yield 1 : 1-dimethyl-2 : 4-dihydrobenzene (XVII.) (*Journ. Chem. Soc.*, 1902, lxxxi., 832). But though the hydrocarbon obtained by the action of quinoline on the dibromodimethylhexahydrobenzene had the odour and gave the colour reaction characteristic of 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene, it has been proved by analysis and a study of its oxidation products to be an undoubted mixture of dimethyldihydro- and dimethyltetrahydro-benzenes.

Being under the misapprehension that the dibromodimethylhexahydrobenzene, from which the mixture of hydrocarbons had been prepared, was a homogeneous

substance, the oxidation products expected were *as*-dimethylsuccinic acid, resulting from the oxidation of the dimethyldihydrobenzene, and *ββ*-dimethyladipic acid, from the oxidation of the dimethyltetrahydrobenzene.

$$CMe_2<\begin{matrix}CH_2.CHBr\\CH_2-CH_2\end{matrix}>CHBr \rightarrow$$
$$\rightarrow CMe_2<\begin{matrix}CH_2-CH\\CH_2.CH_2\end{matrix}>CH \rightarrow$$
$$\rightarrow CMe_2<\begin{matrix}CH_2.CO_2H\\CH_2.CH_2.CO_2H\end{matrix}$$

Instead there were actually obtained *aa*-dimethyladipic and *as*-dimethylsuccinic acids. This at once proved that the tetrahydrobenzene contained in the mixture of hydrocarbons must have been 1 : 1-dimethyl-Δ^2-tetrahydrobenzene, and therefore that the supposed 1 : 1-dimethyl-Δ^3-tetrahydrobenzene, which formed the starting-point of this investigation, was not a homogeneous substance, but consisted of a mixture of 1 : 1-dimethyl-Δ^2-tetrahydrobenzene and 1 : 1-dimethyl-Δ^3-tetrahydrobenzene. If this were so, then on oxidation a mixture of *aa*- and *ββ*-dimethyladipic acids would be obtained, and, as it had been

$$CMe_2<\begin{matrix}CH_2-CH\\CH_2.CH_2\end{matrix}>CH \rightarrow CMe_2<\begin{matrix}CH_2.CO_2H\\CH_2.CH_2.CO_2H\end{matrix}$$

$$CMe_2<\begin{matrix}CH=CH\\CH_2.CH_2\end{matrix}>CH_2 \rightarrow$$
$$\rightarrow CMe_2<\begin{matrix}CO_2H\\CH_2.CH_2.CH_2.CO_2H\end{matrix}$$

found possible, contrary to the statement of Blanc (*Bull. Soc. Chim.*, 1905, [iii.], xxxiii., 889), to separate these two acids (Crossley and Renouf, *Journ. Chem. Soc.*, 1906, lxxxix., 1552), a further quantity of 20 grms. of dimethyltetrahydrobenzene (*Ibid.*, 1905, lxxxvii., 1499) was prepared and oxidised with potassium permanganate (*Ibid.*, p. 1502). There was no difficulty in proving that the solid product obtained consisted of a mixture of *aa*- and *ββ*-dimethyladipic acids, in which the latter largely predominated, thus proving definitely the correctness of the above inference regarding the composition of the substance previously described as 1 : 1-dimethyl-Δ^3-tetrahydrobenzene.

It follows from the above evidence that the supposed 3 : 4-dibromo-1 : 1-dimethyl-hexahydrobenzene (Crossley and Renouf, *Journ. Chem. Soc.*, 1905, lxxxvii., 1501) is a mixture of this substance with the corresponding 2 : 3-dibromo-derivative. When treated with quinoline the former (XVIII.) loses the elements of hydrogen bromide to

$$CMe_2<\begin{matrix}CH_2.CHBr\\CH_2-CH_2\end{matrix}>CHBr \rightarrow CMe_2<\begin{matrix}CH:CH\\CH_2.CH\end{matrix}>CH.$$
XVIII.

give 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene, which forms the main portion of the resulting mixture of hydrocarbons. But in the case of 2 : 3-dibromo-1 : 1-dimethyl-hexahydrobenzene (XIX.) the removal of the hydrogen bromide

$$CMe_2<\begin{matrix}CHBr.CHBr\\CH_2-CH_2\end{matrix}>CH_2 \rightarrow CMe_2<\begin{matrix}C=C\\CH_2.CH_2\end{matrix}>CH_2$$
XIX. XX.

or—

$$CMe_2<\begin{matrix}CH=CH\\CH_2.CH_2\end{matrix}>CH_2.$$

cannot take place in an exactly similar manner, because the carbon atom to which the *gem*-dimethyl group is attached has no hydrogen atoms in connection with it. The reaction might take place, giving rise to a substance of Formula XX. containing a treble bond, or the two bromine atoms might be alone removed, possibly as a quinoline bromide. The former suggestion does not seem probable, because, although the hydrocarbon would give *aa*-dimethyladipic acid on oxidation, it would be isomeric with dimethyldihydrobenzene, but analysis showed the substance to be a mixture of dimethyldihydro- and dimethyltetrahydro-benzenes. In the latter case 1 : 1-dimethyl-Δ^2-tetrahydrobenzene would result, which would also give *aa*-dimethyladipic acid on oxidation, and, furthermore, its presence would be in agreement with the analytical data.

(To be continued).

ON THE NATURE OF VALENCY.*

By Prof. W. J. POPE and W. BARLOW.

THE modern developments of chemistry and crystallography indicate with ever increasing distinctness that the chemical atom, even when its individuality is shrouded by combination with other and different atoms, exhibits characteristics which are essentially its own and which are discernible in the compounds into which it enters. As chief among the attributes which an atom exhibits when present as a constituent of a compound molecule may be noted (1) its mass, (2) its space-occupying property or characteristic volume, and (3) its position property, or power of retaining occupation of a definite domain with respect to neighbouring atoms.

Nothing need here be said concerning the conservation of atomic mass; with regard to (2), the space-occupying property or characteristic volume of the atom, it may be remarked that the work done on molecular volumes has all had for its object the definition of conditions under which the atom of any particular element occupies the same volume when contained in different molecular complexes. The conception is thus involved that if a series of substances could be examined under absolutely corresponding conditions it would be found that those atoms common to the several substances would occupy the same absolute volume throughout the series. We have endeavoured to show in our work that if two elements are common constituents of a number of compounds, the relation between the volumes occupied by the atoms of those two elements remains practically constant during the passage from any one to any other compound of the series. As to (3), the conclusion that in a compound substance each component atom appropriates a certain domain of fixed position with respect to the other atoms composing the molecule, is established by the facts of stereochemistry and by the crystallographic facts connected with isomorphism and with morphotropic relationships.

A fourth attribute of the atom may now be mentioned, namely, the shape assumed by its domain. It is obvious that the second and third properties of the atom, those concerned with its volume and its arrangement, must play a large part in defining the shape of the space which it appropriates in a compound substance. Given the relative situations of the centres of the atomic domains and the relative volumes of those domains, the problem involved in the shape of the latter resolves itself into that of partitioning the space occupied by the substance, without leaving interstices, so as to allot to each atom its own polyhedral cell or domain throughout which its influence is predominant.

The object of the present communication is to demonstrate the possibility, in a great number of cases, of arriving at perfectly definite conclusions concerning the last three attributes referred to by using the data accumulated by chemists and crystallographers, and that a consequence of this is to prove that the fundamental valency of an element represents very approximately the number of units of volume contained in the polyhedral cell which constitutes the domain of its atom in any molecular assemblage. Valency thus stands revealed as primarily a simple volume relation, and this result is found to be in harmony with the various aspects of valency as illustrated by the composition and constitution of both organic and inorganic

* Paper forming the basis of a Discussion on this subject at the Leicester Meeting of the British Association (Section B), 1907.

compounds. The simplest possible assumption as to the form of the atomic domain or the sphere of atomic influence leads to results which are in most cases in immediate concordance with the experimentally determined facts, and, in other cases, leads to such a close approximation to concordance as indicates that any requisite modifying hypothesis is but subsidiary in character.

It is now known that all crystalline substances are distinguished by possessing homogeneity of structure, a homogeneous structure being described as one in which corresponding points continually recur about each of which the distribution of parts is the same. A number of facts indicate that in a crystalline substance the relative movements of the atoms or molecules composing the substance are performed about centres which occupy fixed positions; the atoms may indeed for most purposes be regarded as centres of attraction and repulsion, and the crystalline structure then becomes an equilibrium arrangement of such centres.

In the crystalline structure assumed by an element, provided that the identical component atoms do not form groups or molecular aggregates the constituent atoms of

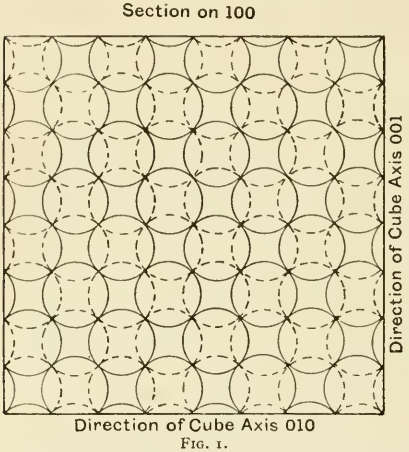


Fig. 1.

which have diverse situations, the polyhedral spaces appropriated by the atoms will be all alike; the simplest possible assumption which can be made as to the shape of these spaces or spheres of atomic influence is that they depart as little as possible from sphericity. The polyhedral cells must fill space without leaving interstices, and, according to the assumption referred to, the centres of the identical polyhedral cells will be those of the centres of a closest-packed assemblage of equal spheres.

As is well known, there are two varieties of homogeneous arrangement of equal spheres in closest-packing, all other equally close-packed arrangements being formed by intimate interstratification of these; they are distinguished as the cubic and the hexagonal closest-packed arrangements respectively. The cubic arrangement possesses holohedral cubic crystalline symmetry, and its plan, parallel to a cube face, consists of two alternating sections as shown in continuous and broken circles respectively in Fig. 1; the plan parallel to an octahedron face consists of three consecutive sections which are shown respectively as heavy, light, and broken circles in Fig. 2.

The hexagonal arrangement possesses holohedral hexagonal symmetry, and its plan on a plane parallel to the principal plane of symmetry consists of the two sections shown in Fig. 3; the axial ratio of the hexagonal closest-packed assemblage of equal spheres is either $a : c = 1 : 0{\cdot}8165$ or $1 : 1{\cdot}4142$, according to the direction selected for the axis a.

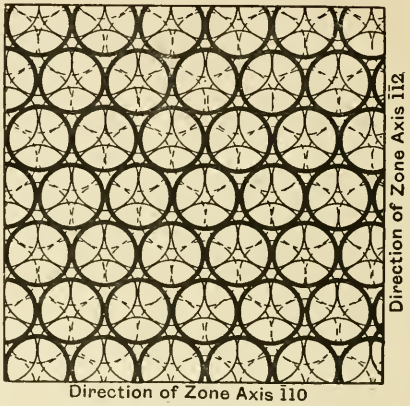


Fig. 2.

If these two closest-packed arrangements are built up of elastic and deformable, but incompressible, spheres, and the completed assemblages are subjected to sufficient uniform pressure from all sides to squeeze the spheres into the shape of polyhedra, all interstitial space will be eliminated, but the symmetry and relative dimensions of the arrangements will be preserved. Arrangements thus modified represent equilibrium assemblages of centres of attraction and repulsion in the cases where all these centres are similar.

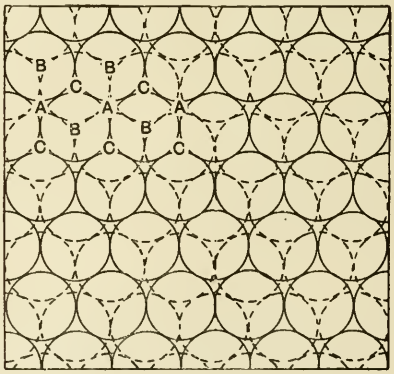


Fig. 3.

A crystalline element in which no molecular aggregation of the similar atoms occurs should thus exhibit holohedral cubic or hexagonal symmetry, and, in the latter case, the axial ratio would have one of the values stated above; that this is so is confirmed by the fact that of the 40 known

crystalline forms of the elements 20 are cubic and 14 are hexagonal, and that, in the cases of the latter, the axial ratios approximate to the theoretical values stated.

About six crystalline forms of elements are known which are neither cubic nor hexagonal; the operation of some factor additional to those already referred to must be assumed to account for their occurrence. Suppose that in the building up of the two closest-packed assemblages of equal spheres described, a form of aggregation of the spheres occurs which is comparable to molecular aggregation; unless this aggregation is strictly compatible with the formation of a cubic or hexagonal closest-packed assemblage, as the case may be, the packed assemblage

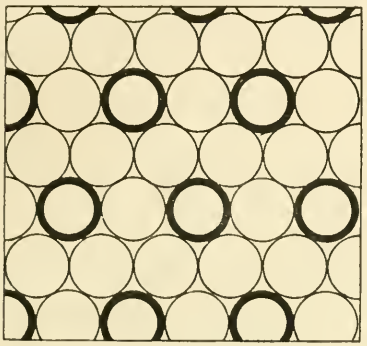


Fig. 4*a*.

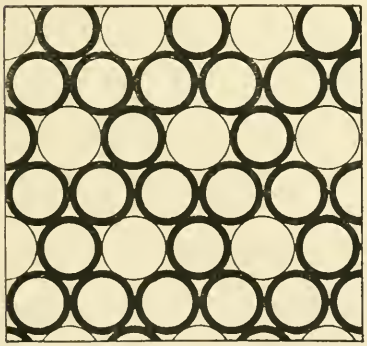


Fig. 4*b*.

will be one in which certain component spheres, homogeneously arranged, will receive slightly different treatment from the others. The conditions thus established could be simulated, so far as the general or crystallographic symmetry is concerned, by building up the appropriate assemblages from spheres possessed of slight polarity, from figures differing slightly from perfect spheres, or from two or more kinds of spheres nearly equal in size and present in definite numerical proportion. The arrangement, or the "marshalling," of the cubic or hexagonal closest-packed assemblage would still be retained, but the resultant assemblage would not be identical in symmetry and dimensions with that produced by using equal spheres.

The crystalline forms of those elements which are neither cubic nor hexagonal can be simulated in the manner thus indicated; they are, in fact, all either pseudo-cubic or pseudo-hexagonal. Thus, the monosymmetric form of sulphur showing $a : b : c = 0{\cdot}9958 : 1 : 0{\cdot}9998$, $\beta = 95°46'$, is obviously pseudo-cubic, and the orthorombic iodine, which shows the axial ratios, $a : b : c = 0{\cdot}6644 : 1 : 1{\cdot}3653$, is also pseudo-cubic because the axial ratios given are almost precisely in the ratio of $a : b : c = 2 : 3 : 4$.

On turning next to binary compounds composed of two elements of the same valency, it is found that practically all of these are either cubic or hexagonal in crystalline form. The following is a complete list of the axial ratios of the known hexagonal members of this class, from which it will be seen that all approximate very closely to the form of axial ratios, $a : c = 1 : 0{\cdot}8165$ or $1 : 2 \times 0{\cdot}8165$, of the hexagonal closest-packed assemblage of equal spheres. The cubic and hexagonal forms of the binary compounds of two elements of the same valency are, however, not all holohedral in crystalline symmetry.

BeO	..	..	..	$a : c = 1 : 1{\cdot}6305$
ZnO	..	..	..	$a : c = 1 : 1{\cdot}6077$
ZnS	..	..	..	$a : c = 1 : 0{\cdot}8175$
CdS	..	..	..	$a : c = 1 : 0{\cdot}8109$
AgI	..	..	..	$a : c = 1 : 0{\cdot}8196$

It is convenient to term the space occupied by each sphere in the uncompressed assemblage plus a proportionate

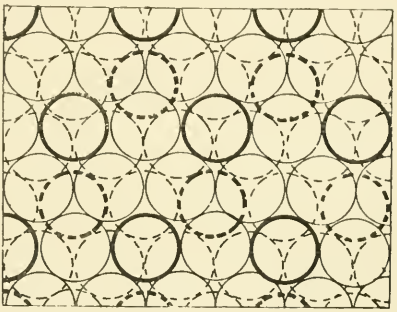


Fig. 5.

share of the interstitial space, or by each polyhedron in the compressed assemblage, the sphere of influence of an atom of the element concerned. By assigning to the two constituent elements of any of the binary compounds just mentioned spheres of atomic influence of approximately the same volume, it is obvious that assemblages may be built up which will exhibit the axial ratios quoted above. Homogeneous assemblages representative of the cubic or hexagonal binary compounds in question can be constructed from spheres of two kinds, but of approximately equal volume, present in equal numbers; in every case the hemihedrism shown by the binary compound can be accounted for by the slight difference in size between the spheres of atomic influence of the two elements concerned. This has been worked out in detail in the case of the gyrohedrally hemihedral cubic alkali halogen salts and the hemimorphously hexagonal silver iodide. The assemblages thus constructed present geometrical properties which are entirely in harmony with corresponding physical properties of the crystalline material. The cleavage, twinning, and gliding of the cubic alkali halogen salts and the dimorphism of silver iodide are quite precisely paralleled by corresponding properties of the assemblages suggested as representing the crystalline structures of these salts.

The crystal structure of the binary compound is, in all

the preceding cases, derived by packing together triangularly arranged layers of the same pattern in either cubic or hexagonal symmetry; these layers are made up of two sorts of spheres and are of two kinds, as indicated in Fig. 4, *a* and *b*. One sort of sphere, say that marked heavily, represents the sphere of influence of the metallic atom; the other, which is marked lightly, represents the other element present in the binary compound. Since in the first layer, say Fig. 4*a*, only one-fourth of the total number of spheres represent metallic atoms, it should be possible to derive assemblages representing the tri-halogen compounds of the alkali metals, such as RbI_3, by arranging identical layers of this kind in close-packing. An appropriate mode of packing such layers is shown in Fig. 5, which represents an assemblage in which three principal dimensions can be distinguished as lying in three principal directions mutually at right angles: the values of the corresponding dimensions in these directions, if all the spheres are equal, are as—

$$a : b : c = 1 : 2\sqrt{\tfrac{2}{3}} : \sqrt{\tfrac{2}{3}}$$
$$= 0{\cdot}6124 : 1 : 1{\cdot}0608.$$

These values approximate to those obtained as the axial ratios of the orthorhombic tri-halogen compounds of the alkali metals, a few of which are next stated :—

	a :	*b* :	*c*	*x* :	*y* :	*z*
RbI_3	0·6858 :	1 :	1·1234	1·1875 :	1·7316 :	1·9452
CsI_3	0·6825 :	1 :	1·1051	1·1901 :	1·7440 :	1·9273
TlI_3	0·6828 :	1 :	1·1217	1·1846 :	1·7350 :	1·9461
Ideal values	0·6124 :	1 :	1·0608	1·1224 :	1·8239 :	1·9443

The values last quoted, conveniently termed the ideal values, refer to the structure composed of two kinds of spheres of equal size, the one kind being three times as numerous as the other. (The values *x*, *y* and *z* given in the table represent the so-called equivalence parameters: they satisfy the conditions that $x : y : z = a : b : c$ and $x \times y \times z = W$; W being the sum of the valencies of the atoms composing the molecule). If the two kinds of sphere are not of exactly the same size, it can be shown that the values of *a* or *x* should be greater according as the difference between the two sizes is greater, and that the minimum value, 0·6124 or 1·1234, would only be attained with two kinds of spheres of identical volume. Similarly the magnitude *y* should assume a maximum value in the ideal assemblage, and any difference in volume between the two kinds of spheres should result in a diminution of the *y* value to less than the maximum value of 1·8239. These conditions are fulfilled in the cases of all the measured compounds, 16 in number, of the type under discussion; the *x* value is always greater, and the *y* value always less, than those holding for the ideal assemblage of equal spheres.

From a consideration of the axial ratios and the equivalence parameters of the alkali trihalides it is concluded that the spheres of atomic influence of the monovalent elements concerned have not exactly the same volumes, but that the relation in size is of the following kind :—

Cl less than Br and Br less than I.
K less than Rb, Rb nearly equal to Tl, and less than Cs.

This kind of relation is found to hold consistently throughout numbers of compounds, and is traceable in series of quite different types to the substances under discussion. Thus Tutton has recently shown that the orthorhombic rubidium and thallous sulphates (or selenates) exhibit axial ratios which are more nearly alike than those of the corresponding salts of potassium, rubidium, and cæsium. Evidence is also available that the sphere of atomic influence of fluorine is smaller than that of chlorine, and in accordance with this it is to be noted that the compounds SF_5 and SCl_4 are those in which sulphur is combined with the maximum proportion of the halogen element.

(To be continued).

NOTICES OF BOOKS.

A Text-book of Botany and Pharmacognosy. By Henry Kraemer, Ph.B., Ph.D. Second Edition. Philadelphia and London: J. B. Lippincott Company.

In the first part of this book the distinguishing characters of the main groups of plants, their morphology and histology, are discussed in detail, a certain amount of plant physiology being also introduced. The points in which students of pharmacy and medicine are specially interested are emphasised, and a chapter is devoted to the cultivation of medicinal plants; full lists are given of those medicinal plants which grow wild in America and of those which already are, or might profitably be, cultivated. The second section deals with pharmacognosy, and opens with descriptions of crude drugs, their constituents and adulterants, together with directions for collecting and preserving them. In the second chapter of this part a system of classification of powdered drugs and foods is given, and their identification is made as simple as possible, so that analysts will find that the book is a valuable aid to them in this difficult and important branch of their work. The third section gives a short account of the reagents required for microscopical work and the preparation and staining of sections. The book is particularly fully and well illustrated, and for students of pharmacy and medicine it has a great value as a comprehensive text-book.

Forty-third Annual Report on Alkali, &c., Works. By the Chief Inspector. London: Wyman and Sons. Edinburgh: Oliver and Boyd. Dublin: E. Ponsonby. 1907.

The general and detailed reports of the work done during 1906 under the provisions of the Alkali, &c., Works Regulations Acts are supplemented in this volume by a full account of researches on the constitution of ammoniacal liquors. It has been found that in the main the methods hitherto adopted have given satisfactory results, and they are still employed with some slight modifications. The process for the estimation of thiocyanate has, however, undergone a complete revision, and a method has now been worked out which is decidedly more accurate than the original procedure, and has the advantage of being quickly performed. Full details of this new method are included in the Reports. The temperature of carbonisation in coke ovens and gas retorts has also been the subject of investigation, and reproductions are given of graphical records from one of the coke ovens in Brackley Colliery, as well as the temperature charts from a paper read by Mr. J. Bond, engineer and manager of the Southport Corporation Gas Works, before the Institution of Gas Engineers, in May, 1905.

Denatured or Industrial Alcohol. By Rufus Frost Herrick. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

In January, 1907, a law permitting the use of tax-free denatured alcohol came into force in the United States, and accordingly this book will have a special interest for American chemists, engineers, and manufacturers, and even for the general public. The author gives a full account of the manufacture, distillation, and rectification of alcohol, and describes methods of examining it for impurities, while its use as an illuminant is carefully compared with that of acetylene. In describing the various burners, stoves, &c., which are adapted for alcohol, and the machines in which it is used as a source of power, the author has been obliged to illustrate chiefly foreign machinery, Germany especially having been in the forefront in developing this kind of apparatus, although now the internal revenue tax has been removed in America in all probability the next few years will see great increases in its employment in the United States. A considerable part of the book is devoted to the laws and regulations for

denatured alcohol now in force, and a useful list of patents relating to its manufacture, and to various modifications of distilling apparatus is included.

Traité Complet d'Analyse Chimique Appliquée aux Essaies Industriels. ("Treatise on the Chemical Analysis of Industrial Products") By J. Post and B. Neumann. Translated by Dr. L. Gautier. Vol. I., Part I. Paris: A. Hermann. 1907.

The Second French Edition of this comprehensive treatise has been prepared from the enlarged Third German Edition, now in course of publication, by Dr. Gautier, who has made some important additions to the text. The first part of Vol. I. contains sections on the analysis of water by Dr. J. H. Vogel, on fuels by Dr. H. Langbein, and on pyrometry and the analysis of gases from furnaces, chimneys, mines, &c., by Prof. Neumann. The illustrations of the original have been carefully reproduced, and the work will be cordially welcomed by French technical chemists.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 2. July 8, 1907.

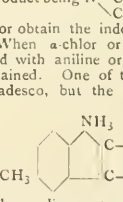
Preparation and Properties of Borides of Iron, Fe_2B and FeB_2.—Binet du Jassonneix.—Mixtures of varying proportions of iron and boron were heated in a magnesia boat in a porcelain tube through which a current of hydrogen was passed. Mixtures which are infusible at the temperature at which porcelain begins to soften were heated in magnesia crucibles in the electric furnace. The melts obtained looked crystalline when up to 7 per cent of boron was present. The surface and fracture showed long prismatic needles, which could be isolated by allowing cold dilute hydrochloric acid to act upon the melt for some time. These crystals have the formula Fe_2B. When the percentage of boron was above 7 the crystallisation appeared less regular. Melts with about 9 per cent of boron appeared homogeneous, and were completely dissolved by cold hydrochloric acid. The boride Fe_2B consists of steel-grey crystals; its density at 18° is 7·37; it oxidises in dry air only at a red heat, but in damp air it is rapidly altered; it dissolves very slowly in dilute or concentrated hydrochloric and sulphuric acids when warmed, but is not attacked by the cold acids. Warm dilute nitric acid dissolves it, and the concentrated acid attacks it very rapidly in the cold. The compound FeB_2 when prepared in an electric arc furnace contains a large amount of carbon boride. When most of this is removed a metallic powder is obtained; it is not attacked either by hot or cold dilute hydrochloric acid; the concentrated acid slowly attacks it when heated; nitric acid dissolves it easily, leaving a residue of carbon boride; it is oxidised slowly in the air.

Direct Oxidation of Toluene by Catalysis.—Paul Woog.—When a current of air containing toluene is passed over a hot platinised mass, made by impregnating fragments of meerschaum (previously washed with acids) with a platinum salt, then reducing the latter and washing, energetic oxidation takes place, and the toluene is completely burnt to carbon dioxide and water, provided that the temperature is sufficiently high to prevent the toluene condensing. When iron oxide is used as catalyser at temperatures from 175—300° benzaldehyde is regularly formed, the best yield being obtained when the tube is raised to a temperature of 280° and the toluene to 90°. Above 280° the iron oxide becomes incandescent and some carbonaceous matter is obtained. Under the same conditions nickel oxide gives rise to benzaldehyde at 150°. Above 230° small quantities of phenolic substances are obtained, and may be detected by their smell and by means of Millon's reagent. The nickel oxide becomes incandescent at 270°. Copper oxide gives a certain amount of benzaldehyde, but most of the toluene is burnt, the oxide becoming incandescent above 250°. With manganese dioxide the hydrocarbon is completely burnt. If carbon, in the form of coke, is used as a catalyser, a little aldehyde is produced at 200°, but the chief product of the oxidation is benzoic acid, large quantities being formed at 370°.

New Method of Preparing Amino-alcohols with Primary Alcoholic Function.—H. Gault.—The author has prepared ethyl glycocollate, benzyl, phenyl, *m*- and *p*-tolyl, methyl phenyl aminoacetic esters, and β-diethylaminopropionic ester by the direct condensation (except in the first case) of ethyl chloracetate or β-chlorpropionate with the corresponding amines—a method which gives excellent results, the amino-ester being obtained quantitatively. When these esters are reduced by sodium and absolute alcohol, the directions of Bouveault and Blanc being carefully followed, varying yields of the corresponding amino-alcohols are obtained, except in the case of ethyl glycocollate and ethyl *m*- and *p*-tolyl acetates, and thus, though the reduction of these esters is not effected when the amine function is primary, this method may with advantage be employed to prepare primary amino-alcohols when the amine function is secondary or tertiary.

Asymmetric Derivatives of Hexane-diol 1 : 6. Heptamethylene Glycol. — R. Dionneau.—To prepare the bromo-ethers of hexane-diol of the formula $RO(CH_2)_6Br$, it is best to allow one molecule of alkaline alcoholate to react upon one molecule of dibromohexane in anhydrous ether, $CH_3ONa + Br(CH_2)_6Br = NaBr + CH_3O(CH_2)_6Br$. The reaction occurs at the temperature of the room, and the crystals of sodium bromide are deposited at the end of a day. When they begin to appear, the mixture is warmed gently and the ether layer distilled off. At 112° methoxybromohexane 1 : 6 distils over. The magnesium derivative, $BrMg(CH_2)_6OCH_3$, when treated with bromomethyl ether, $BrCH_2OCH_3$, gives the dimethyl derivative of heptane diol, $CH_3O(CH_2)_7OCH_3$. This, when heated to 100° with hydrobromic acid, gives dibromoheptane 1 : 7, from which diphenoxyheptane can be prepared by the action of sodium phenolate. Dibromoheptane when treated with silver acetate is transformed into the diacetic ether, which gives heptamethylene glycol when distilled over soda-lime.

Action of Halogen Derivatives of Acetones upon Aromatic Amines.—A. Richard.—When monochlordimethyl acetone reacts with two molecules of aniline warmed on a water-bath, aniline chlorhydrate is formed, and a viscous brown substance, which dissolves in hydrochloric acid and in alcohol. If the alcoholic solution is thrown into cold water a chesnut-brown precipitate is formed, which appears to be a phenyl acetone amine of the formula $N\begin{cases}H\\C_6H_5\\CH_2—CO—CH_3\end{cases}$. The reaction occurs similarly when one of the three toluidines is substituted for aniline, the product being $N\begin{cases}H\\C_6H_4.CH_3\\CH_2—CO—CH_3\end{cases}$. In no case did the author obtain the indolic derivative described by Vladesco. When α-chlor or α-brom methyl ethyl acetone is heated with aniline or *p*-toluidine, crystalline products are obtained. One of these has already been described by Vladesco, but the other has the formula $C_{10}H_{11}N$, or—



Apparently, at the ordinary temperature the reaction which occurs is a double decomposition. The halogen combines with one atom of the hydrogen of the amine employed, giving a hydracid which forms a salt of the

amine, while the ketone residue takes the place of the hydrogen atom. If this ketonic amine is heated, and if the group $-N<^{H}_{R}$ is in the secondary position with regard to the group —CO— (as in the case of α-chlormethyl ethyl acetone), a more extensive condensation occurs, and one molecule of water and an indol derivative are formed.

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Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 11, 1907.

Anodic Disturbances in the Electrolysis of Fused Salts.—K. Arndt and K. Willner.—When a current is passed through fused barium chloride in a porcelain crucible, using thick iron wire as cathode and a carbon rod as anode, the resistance of the bath steadily increases after a few minutes, and the evolution of chlorine ceases. The same thing happens when strontium chloride is similarly treated, while calcium chloride can readily be electrolysed without exhibiting the phenomenon. If the anode is moved about it is possible to cause more chlorine to be generated. This difference in the behaviour of barium and strontium, on the one hand, and calcium on the other, cannot be ascribed to the higher melting-points of the two first elements, because the disturbance does not occur when calcium chloride is artifically superheated; nor can it be explained by the difference in the conductivity of the salts, which, though considerable, is not sufficiently large to cause the phenomenon. It was found, however, that the carbon was surrounded by a salt crust, which contained small quantities of silicic acid. This must have been derived from the crucible, for the strontium chloride used contained only 0·02 per cent silicic acid. Thus, when the melt became alkaline it attacked the porcelain, yielding silicates. When a crucible made by a substance containing no silica (*e.g.*, magnesia) was used, the resistance of the bath, although it rose for a moment, sank again, and then remained normal, and metallic strontium was formed in a compact mass. The introduction of a small amount of silica at once increased the resistance. Hence there can be no doubt that the formation of a badly conducting layer of silicic acid is the true cause of the anodic disturbance. Fused calcium chloride dissolves about 4 per cent of silica, while strontium chloride takes up much less. Also the more strongly alkaline strontium attacks the crucible more.

Proof of Divalence of Beryllium. Beryllium Picrate.—B. Glassmann.—When pure picric acid is dissolved in water, warmed, neutralised with beryllium carbonate, filtered, and evaporated to crystallisation, a yellow picrate crystallises out. When dried in air and analysed the formula is found to be $[C_6H_2(NO_2)_3O]_2Be+3H_2O$. If this picrate is treated with ether and dried at 50° it gives up one molecule of water. The molecular weight of the anhydrous picrate was determined by the freezing point method in acetophenone, care being taken that the latter was absolutely free from water. The molecular weight was found in two experiments to be 465 and 471·1, while the calculated value is 465·1. Thus the divalence of beryllium is confirmed by this work. When the anhydrous picrate is treated with water it gives a basic picrate of the formula $[C_6H_2(NO_2)_3O]_2Be.2Be(OH)_2$.

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2491.

COPPER MIRRORS.*

By F. D. CHATTAWAY.

The importance from the point of view of the health of the workpeople of obtaining a substitute for the tin amalgam used in the manufacture of mirrors has led many chemists to study the conditions under which metals are deposited from aqueous solution. These investigations have, however, usually had for their object the preparation of a liquid which would deposit a uniform and coherent layer of silver over a large glass surface at the ordinary temperature. Liebig was the first to solve this problem satisfactorily, and his method in which milk sugar is the reducing agent was formerly extensively used.

Other metals are not so easily deposited, and copper, which from its close relationship with silver one would expect to behave similarly, has never been observed to be so laid upon glass. Although copper mirrors have never been obtained by deposition of the metal from an aqueous solution, Faraday (*Phil. Trans.*, 1857, p. 145), about the time when silver mirrors were attracting much attention, made the interesting observation that a mirror-like deposit could be obtained by dissolving a little oxide of copper in olive oil and heating plates of glass in a bath of this liquid up to the temperature at which the oil decomposes. The mirrors, however, obtained by Faraday's method, if of any size, are liable to be stained or discoloured in patches by decomposition products of the oil, and they are, moreover, generally lacking in brilliancy. Further, as the deposition of the metal only takes place when the oil decomposes, the process is excessively disagreeable to carry out; and since the oil is spoiled it is also somewhat costly.

In the course of an investigation on the oxidation of aromatic hydrazines, the author made the observation that when solutions of cupric oxide are reduced by these compounds the metal is deposited upon the glass in the form of a brilliant coherent film if clear vessels are used.

The mirrors obtained by this method are very beautiful, as they show the lustrous red colour of burnished copper, and are as perfect in reflecting surface and as uniform as the similar mirrors obtained by the deposition of silver.

It seems probable that this method of depositing copper upon glass could receive important application in the production of objects of art.

CAUSES OF THE QUALITY STRENGTH IN WHEATEN FLOUR.†

By A. E. HUMPHRIES.

The Home-grown Wheat Committee of the National Association of British and Irish Millers has for several years been engaged in producing wheats in England which shall yield maximum crops of grain and straw, the wheat to be equal in strength, and therefore in commercial value, to the best imported varieties.

The field of inquiry has been a wide one, and among other things the Committee has sought to ascertain "the ultimate cause of strength in wheat, the nature and source of those constituents which confer on some varieties of wheat the inherent quality of strength, and the power of transmitting it to succeeding generations." It has been proved that though climate and soil influence quality they are not the determining factors in the production of strength, for though the strongest wheats are ordinarily produced in districts where the winters are cold, the summers hot, and the summer rainfall high, certain varieties possess and retain the inherent quality of strength when grown in England. Manuring or early cutting at harvest time has no beneficial effect on quality. Quick growth or rapid maturation is not correlated with strength nor does the percentage of natural moisture in well-harvested wheat indicate it; indeed, in certain cases the addition of water to wheat materially increases its effective baking strength.

The term "strength" has been loosely applied to cover several characteristics. In the view of the Committee it should not be measured by the quantity of water required to make doughs of a standard consistency, nor by the quantity of bread produced per sack of flour used, nor by the way a flour behaves in the dough, but by its capacity for making big, shapely, and therefore well aërated loaves. This definition covers two characteristics; one, a flour's capacity for making gas in yeast fermentation; the other, its capacity when made into dough for retaining the gas so generated.

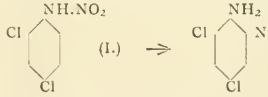
The gas-making power will depend largely on the percentage of natural sugar any given wheat contains and its diastatic capacity. These characteristics vary substantially in different wheats. The baker can, and does, influence the quantity of gas generated in baking. The retention of gas when made involves complex problems.

The percentages of total nitrogen, gluten, gliadin, and amyloids do not correctly indicate the relative strengths of various flours. The theory that strength depends on a correct ratio between gliadin and glutenin is untenable. Professor Wood's suggestion that the gas-retaining power of a dough depends on its ratio of protein to salts is worthy of the closest attention in view of the fact that the physical, as distinct from the chemical, properties of proteins are profoundly affected by small quantities of acids, alkalis, and salts.

THE TRANSFORMATION OF AROMATIC NITROAMINES AND ALLIED SUBSTANCES, AND ITS RELATION TO SUBSTITUTION IN BENZENE DERIVATIVES.*

I. *Nitroamines.* (*With* W. W. Reed, B.Sc.).

A detailed study of the conditions governing the transformation of 2 : 4-dichloro 1-nitroaminobenzene (I.) (Orton, *Trans. Chem. Soc.*, 1902, lxxxi., 802) into the isomeric 2 : 4-dichloro-6-nitroaniline (II.) has been made:—



This nitroamine was chosen for particular study in preference to others, having different positions vacant (ortho and para relative to the group, $NH.NO_2$) into which the nitro-group may "wander," on account of the ease of its preparation (Orton, *Ber.*, 1907, xl., 370), and the non-basic character of the nitroaniline, of the above constitution, which is produced in the isomeric change. In testing the effect of minute quantities of acids as transforming agents it is of great importance that the aniline should not be able to unite with the reagent, which would thus be withdrawn from the sphere of action.

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

† Paper forming the basis of a Discussion on this subject at the Leicester Meeting of the British Association (Section B), 1907.

* Report of the Committee, consisting of Prof. F. S. Kipping (Chairman), Prof. K. J. P. Orton (Secretary), Dr. S. Ruhemann, Dr. A. Lapworth, and Dr. J. T. Hewitt. Read before the British Association (Section B), Leicester Meeting, 1907.

A particular advantage which this transformation offers, in contrast to many others of a similar type, is due to the fact that the nitroamine is quite colourless, and forms colourless solutions, which may be preserved for long periods, whereas the nitroaniline crystallises in intensely yellow needles and forms highly coloured solutions. Traces of the nitroaniline could thus be recognised, not only in solutions, but also in the crystals of the nitroamine. The conversion of the crystalline nitroamine into the nitroaniline is not merely indicated by a simple change of colour, but by the growth of yellow needles of the nitroaniline, apparently out of the colourless nitroamine—a process which can be readily followed photographically. This phenomenon, which can be demonstrated with a single crystal of the nitroamine, has allowed of the testing of the effect of single (necessary gaseous) reagents as transforming agents in the absence of all solvent.

The nitroamine was dried by sealing it up with phosphorus pentoxide in glass tubes. When thus entirely freed from water the substance acquires greater stability, and loses a remarkable sensitiveness to light, which necessitates the use of a dark room when aqueous solutions are employed.

After seven days' drying in this manner the tubes were opened, the reagent introduced, and the tube re-sealed. The reagent, which was in most cases in aqueous solution 0·1 to 0·2 cc.), was enclosed in a small tube, and was separated from the dried nitroamine by a column of phosphorus pentoxide five to six inches in length. The water slowly evaporated, and was absorbed by the pentoxide, the gaseous reagent, now anhydrous, diffusing to the region containing the nitroamine, of which at most one or two crystals (plates or needles) were used. Obviously this procedure admits only of the use of reagents which are not changed by prolonged contact with phosphorus pentoxide.

By this means it has been ascertained that hydrogen chloride, bromide, and iodide, nitric acid, chlorine, or bromine can all act as transforming agents. Iodine, hydrogen cyanide (?), sulphur dioxide, carbon dioxide, and methyl iodide are inactive.

Quantitative experiments carried out with hydrogen chloride have revealed the very interesting fact that there is a limiting concentration (partial pressure) below which hydrogen chloride does not initiate the molecular rearrangement. In the case of the nitroamine here dealt with the partial pressure of the hydrogen chloride must be approximately one-thirtieth atmosphere.

The behaviour of the nitroamine with hydrogen chloride in various solvents was investigated, the most instructive results being obtained in aqueous solution. The solution of the nitroamine in pure water can apparently be preserved indefinitely in a dark room, no trace of colour becoming perceptible, notwithstanding the fact that it is easy to perceive the colour communicated by 1/10 mgrm. of the nitroaniline to 100 cc. of the solution; that is, to detect the transformation of 0·1 per cent of the nitroamine. The addition of hydrogen chloride causes transformation, provided that the acid is above a certain concentration. The nitroamine was used at a concentration of V=207 (1 grm. per litre), the concentration of the acid being varied from N to N/1000. In all the solutions but that last mentioned, in which the molecular ratio $C_6H_3Cl_2.NH.NO_2HCl$ was 5/1, the acid was in excess. The presence of the nitroaniline can be detected with certainty at the end of ten minutes in the N solution, and after longer periods down to a concentration of N/200, below which concentration all change ceases. Similar results were obtained with other acids, but, keeping the concentration of the nitroamine constant, the limiting value of the effective concentrations of the acids varies with the strength of the acid.

In the hope of isolating some compound of the acid and the nitroamine, hydrogen chloride, accurately dried, was passed into a solution of the nitroamine in petroleum. A colourless compound separated, which was resolved by solutions of alkalis into the nitroamine and hydrogen chloride, but when kept in a dry atmosphere the compound slowly changed into the nitroaniline.

These remarkable results greatly illuminate the mysterious part played in this type of intramolecular change by the transforming agent (or catalyst), the necessity for the presence of which was first recognised by Armstrong (*Report*, 1899, p. 683; and *cf. Trans. Chem. Soc.*, 1900, lxxvii., 1053).

The deductions to be drawn from these observations may be thus summarised:—

i. No "specific" reagent is required for any given transformation.

ii. The reagent must be capable of combining with the nitroamine. In all probability this union is effected directly with the nitrogen of the NH group, which thus becomes quinquivalent. The additive product in the case of hydrogen chloride has a composition represented by the formula $C_6H_3Cl_2.NH.NO_2.HCl$.

iii. No transformation occurs in aqueous solution when the concentration of the transforming agent is below a certain value (for hydrochloric acid below N/200), the nitroamine being at a dilution of V = 207. The additive compound is apparently completely "hydrolysed" at such dilution.

iv. The additive compound is not formed from gaseous hydrogen chloride and the nitroamine when the pressure of the former is below a certain value—namely, the dissociation pressure of the compound. This pressure is approximately one-thirtieth atmosphere at 15° C.

It has been suggested that the additive compound of the nitroamine and the transforming agent is alone capable of undergoing those further changes, probably through the transitory conversion of the benzene nucleus into a quinonoid form, by which the nitro-group "wanders" from the nitrogen into the nucleus, whereas the simple nitroamine has no such power (see Orton, *Proc. Roy. Soc.*, 1901, lxxi., 153).

II. *The Wandering of Bromine in the Chlorination of Bromoanilines.* (*With* W. W. Reed, B.Sc.).

Although the replacement of bromine by chlorine in anilines (Wegscheiden, *Monatsheft*, xviii., 329; Chattaway and Orton, *Trans. Chem. Soc.*, lxxix., 822), and in bromobenzenediazonium chlorides (Hantzsch, *Ber.*, xxx., 2334), has been observed, the displacement of bromine by chlorine from a given position in the benzene nucleus, followed, however, by a subsequent re-entry in another position, has not been described.

In the chlorination of *p*-bromoaniline, either by the usual method of passing chlorine into a solution in benzene or chloroform, or by the more delicate procedure of adding the requisite quantity of a solution of chlorine, or, finally, by using solutions of the aniline and chlorine (in the correct proportions, $C_6H_4Br.NH_2/2Cl_2$) in 20 per cent hydrochloric acid, the expected 2 : 6-dichloro-4-bromoaniline—

is not alone obtained. It is always mixed with 2 : 4-dibromo-6-chloro- and *s*-trichloro-anilines, and cannot be separated from them. The aniline can, however, be prepared in a pure state by indirect chlorination of the *p*-bromoaniline in chloroform solution with a solution of 2 : 4-dichloroacetylchloraminebenzene in the same solvent, thus:—

$$C_6H_4Br.NH_2 + 2C_6H_3Cl_2.NCl.AC = C_6H_2Cl_2Br.NH_2 + 2C_6H_3Cl_2.NH.AC.$$

Under these conditions displacement of bromine does not occur.

Similar results were obtained by chlorinating 2 : 4-dibromoaniline in hydrochloric acid solution. On subjecting *o*-bromo-, *m*-bromo-, or 2 : 6-dibromo-aniline to a similar treatment no such displacement was observed, each substance yielding a single chloro-derivative.

DYNAMIC ISOMERISM.*

Attention has been directed during the past year mainly to a study of the influence of impurities on the velocity of mutarotation of nitro-camphor. In an earlier series of experiments on glucose it was found that the mutarotation in aqueous solutions could not be retarded by the addition of either acids or alkalis (Lowry, *Trans. Chem. Soc.*, 1903, lxxxiii., 1314—1323): the isomeric change thus appeared to be due to a direct interaction between the sugar and the water of low conductivity which formed the solvent. In the case of nitrocamphor dissolved in chloroform it has been found possible to check the mutarotation by the addition of N 100 acetic acid, and to stop it altogether during a period of three weeks by the addition of N 1000 trichloracetic acid. The experiments, therefore, afford valuable confirmation of the view already arrived at, that the isomeric change which usually takes place when nitrocamphor is dissolved in chloroform or benzene does not occur spontaneously, but is conditioned by the presence of *minute traces of alkaline impurities* (*Trans.*, 1899, lxxv., 221; *Report*, 1904, p. 196).

Experiments were made to determine quantitatively the effects produced by these impurities. Sodium ethoxide, added to an alcoholic solution of nitrocamphor, was found to produce an acceleration very similar to that which results from the addition of caustic potash to an aqueous solution of glucose; the mutarotation in presence of N 1000 NaOEt was complete in about a quarter of an hour, with N/10,000 NaOEt in about three hours, and a slight acceleration could be detected in presence of N/100,000 NaOEt. The normal period of the isomeric change in absolute alcohol at 20° C. is about six hours, but the change is greatly accelerated by the addition of a little water. The velocity of change in alcohol containing 1 per cent of water was exactly equal to that in a sample of 99·8 per cent alcohol to which sodium ethoxide had been added in a concentration of N/10,000.

Extraordinary effects were produced by the addition of piperidine to solutions of nitrocamphor in benzene. In presence of N 1000 piperidine the mutarotation was complete in two minutes, and even when working as rapidly as possible only two readings of the polarimeter could be obtained before the final value was reached. With N/10,000 piperidine the change was complete in about six minutes, with N 100,000 in an hour, and with N 1,000,000 in about ten hours. With N 10,000,000 piperidine the acceleration of the isomeric change was comparable with that due to the trace of impurity normally present in the purified materials, and no definite observations could be made.

In the case of the N 100,000 solution the molecules are present in the proportion—

Piperidine : nitrocamphor : benzene = 1 : 25,000 : 1,000,000,

and about 2 per cent of the nitrocamphor undergoes change in each minute. It therefore follows that if each molecule of piperidine is able to invert only one molecule of nitrocamphor at a time, it must accomplish 500 such inversions per minute, and unless selectively guided to the nitrocamphor must come in contact also with some 20,000 molecules of benzene.

In view of the remarkable effects produced by the addition of piperidine, it is noteworthy that the addition of aniline is almost without effect. In presence of N/1000 aniline the velocity of isomeric change in a solution of nitrocamphor in benzene was slower than in presence of N/10,000,000 piperidine—a result that was confirmed by a second series of observations; the blank experiment, with benzene only, showed a still slower change, but this result was only achieved by very careful purification of the materials.

The experiments now described are of importance as indicating the conditions under which isomeric change may in general take place. It may be concluded that in neutral solvents, such as benzene and chloroform, no change can occur unless some third substance or impurity is present; the influence of the impurity may be greatly increased by raising the temperature or illuminating with ultra-violet light; but even under these conditions it is probable that isomeric change is not a spontaneous result of the interaction of solvent and solute.

The experimental evidence thus gives no support, but on the contrary is entirely opposed to the existence of the condition of intermolecular "wobble" postulated by Laar in his theory of "tautomerism" (*Ber.*, 1885, xviii., 648—657). It is, moreover, very doubtful whether even the special case of the process of "bond-shifting," or "desmotrophy" (Jacobson, *Ber.*, 1888, xxi., 2628), which does not involve the transference of a mobile hydrogen atom, and which Baly (Stewart and Baly, *Trans. Chem. Soc.*, 1906, lxxxix., 498) has described as "isorropesis," could occur in pure neutral solvents in the absence of a catalytic agent.

In addition to the investigation described above considerable attention has been paid during the past year to the study of the optical properties of dynamic isomerides, and preparations have been made for a detailed examination of the relationship between the absorption spectra of isodynamic compounds and the velocity with which they undergo isomeric change.

* Report of the Committee, consisting of Professor H. E. Armstrong (Chairman), Dr. T. M. Lowry (Secretary), Professor Sydney Young, Dr. J. J. Dobbie, Dr. A. Lapworth, Dr. M. O. Forster, and Dr. C. H. Desch. (Drawn up by the Secretary). Read before the British Association (Section B), Leicester Meeting, 1907.

THE STUDY OF HYDRO-AROMATIC SUBSTANCES.*

(Concluded from p. 79).

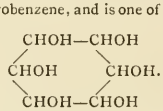
Recent Work on Hydro-aromatic Substances.
By Professor A. W. Crossley.

Hydrocarbons.—The ozonides of hydro-aromatic hydrocarbons (Harries and Nerescheimer, *Ber.*, 1906, xxxix., 2846) produced by the direct addition of ozone to a double bond in a six carbon ring, differ markedly from analogous derivatives obtained from open chain hydrocarbons, or from members of the aromatic series, in being very stable towards water. Thus, the ozonide of 1 : 1 : 3-trimethyl-Δ^3-tetrahydrobenzene (cyclogeraniolene) is with difficulty acted on by water; the ozonide of tetrahydrobenzene is slowly changed by boiling with water, yielding principally adipic acid and small quantities of adipic aldehyde, whereas the ozonide of dihydroxylene does not give any definite products. Furthermore, the ozonides of hydro-aromatic hydrocarbons show irregularities in their composition, for though tetrahydrobenzene ozonide has the normal composition $C_6H_{10}O_3$, the derivatives obtained from 1 : 1 : 3-trimethyl-Δ^3-tetrahydrobenzene appears to contain four atoms of oxygen and to possess a double molecular weight. This alone would not preclude the use of such substances for the determination of the constitution of hydro-aromatic hydrocarbons if they were not so difficult to decompose with water. It has, however, now been ascertained that reduction of the ozonides leads to the production of the same aldehydes or ketones as would be formed by the action of water; or, if very energetic reducing agents are employed, to the corresponding alcohols. But the method

* Report of the Committee, consisting of Dr. E. Divers (Chairman), Prof. A. W. Crossley (Secretary), Prof. W. H. Perkin, Dr. M. O. Forster, and Dr. H. R. Le Sueur. Read before the British Association (Section B), Leicester Meeting, 1907.

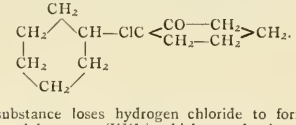
possesses the disadvantage that it is not so easy to make a quantitative estimation of the products as when the decomposition is brought about by water.

Alcohols.—Scyllite, discovered in 1856, by Staedeler in certain cartilaginous fishes, has been further examined by Müller (*Ber.*, 1907, xl., 1821). It has the formula $C_6H_{12}O_6$, forms monoclinic crystals melting in the neighbourhood of 360°, is but slightly soluble in water, is optically inactive, and gives a hexacetyl derivative. It is concluded from this evidence that scyllite is a hexahydroxyhexahydrobenzene, and is one of the inactive forms of inosite.

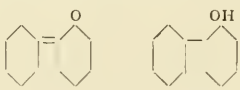


Ketones.—Ketohexahydrobenzene, like phloroglucinol and dihydroresorcin, is capable of existing in two tautomeric forms, either as the ketone or as hydroxy-Δ^1-tetrahydrobenzene, for when heated with acetic anhydride and sodium acetate (Mannich, *Ber.*, 1906, xxxix., 1594) it yields the acetyl derivative of hydroxytetrahydrobenzene. The latter is a colourless oil boiling at 180—182°, and possessing a pleasant fruity odour. It is readily oxidised by potassium permanganate, giving adipic acid, and is hydrolysed by alcoholic potassium hydroxide with regeneration of ketohexahydrobenzene.

Condensation products of a varied nature have been obtained from ketohexahydrobenzene; thus when hydrogen chloride is passed into the pure ketone (Wallach, *Ber.*, 1907, xl., 70) a solid product results, having the formula $C_{12}H_{19}OCl$, and the probable constitution—

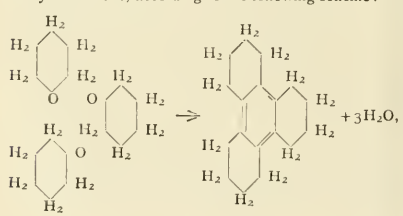


This substance loses hydrogen chloride to form cyclohexenecyclohexanone (XXI.), which on reduction gives the corresponding saturated alcohol (XXII.). From this latter body, by treatment with hydrogen iodide, the fully hydrogenised dicyclohexane or dicyclohexyl, $C_6H_{11}.C_6H_{11}$ is formed.

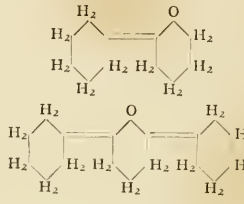


XXI. XXII.

If alcoholic sulphuric acid be used as condensing agent, then Mannich (*Ber.*, 1907, xl., 153) finds that ketohexahydrobenzene behaves similarly to acetone, yielding bodies analogous, as regards method of formation, to mesityl oxide, phorone, and mesitylene, and having the respective formulæ $C_{12}H_{18}O$, $C_{18}H_{26}O$, and $C_{18}H_{24}$. The latter would obviously be produced from three molecules of ketohexahydrobenzene, according to the following scheme:—



which shows it to contain a benzene ring and three hydrogenised benzene rings, and it would therefore be dodecahydrotriphenylene. It crystallises in compact prisms melting at 232—233°, when oxidised with fuming nitric acid yields mellitic acid, and on distillation with zinc-dust in an atmosphere of hydrogen (*Ber.*, 1907, xl., 159) is converted into triphenylene, identical with the substance previously described by Schmidt and Schultz (*Annalen*, 1880, cciii., 135). The ketones $C_{12}H_{18}O$ and $C_{18}H_{26}O$ have probably the following constitutions:—

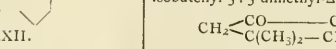


Homologues of ketohexahydrobenzene can be produced by the slow distillation of the anhydrides of substituted pimelic acids, when they lose carbon dioxide. Blanc (*Comptes Rendus*, 1907, cxliv., 143) has by this means prepared from $\beta\beta$-dimethylpimelic anhydride 3-keto-1:1-dimethylhexahydrobenzene (see *ante*), which when reduced with sodium and absolute alcohol gives 3-hydroxy-1:1-dimethylhexahydrobenzene, identical in every respect with the product obtained by Crossley and Renouf (see *ante*) by the reduction of chloroketodimethyltetrahydrobenzene. 3-Keto-1:1:4-trimethylhexahydrobenzene has been prepared by a similar reaction.

1:2-, 1:3-, and 1:4-ketomethylhexahydrobenzenes (Wallach, *Annalen*, 1906, cccxlvi., 249).

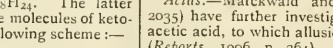
2-Chloro-1-ketohexahydrobenzene is obtained by treating ketohexahydrobenzene suspended in water with chlorine in presence of calcium carbonate (Bouveault and Chereau, *Comptes Rendus*, 1906, cxlii., 1086). When boiled with a strong solution of potassium carbonate it is converted into 2-hydroxy-1-ketohexahydrobenzene, and when treated by Grignard's reaction yields ketomethyl-(ethyl, &c.)-hexahydrobenzene.

A compound isomeric with Pinner's xylitone is formed by the action of sodium ethoxide on a mixture of ethyl acetoacetate and phorone (Knoevenagel and Schwartz, *Ber.*, 1906, xxxix., 3441), and is supposed to be 1-keto-3-isobutenyl-5:5-dimethyl-Δ^2-tetrahydrobenzene. It yields

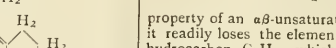


a tetrabromide, and when reduced with sodium and alcohol gives 1-hydroxy-3-isobutyl-5:5-dimethylhexahydrobenzene, which under the influence of phosphorus pentoxide loses water to form 3-isobutenyl-5:5-dimethyl-Δ^1-tetrahydrobenzene.

Acids.—Marckwald and Meth (*Ber.*, 1906, xxxix., 2035) have further investigated 1-methylcyclohexylideneacetic acid, to which allusion was made in the last report. (*Reports*, 1906, p. 264). This acid shows the general



property of an $\alpha\beta$-unsaturated acid, in that, when heated, it readily loses the elements of carbon dioxide to give a hydrocarbon, C_8H_{14}, which is optically inactive, and has already been proved by Wallach to be 1-methyl-4-ethylenehexahydrobenzene,—



Further, as is well known, the bromo-additive compounds of $\alpha\beta$-unsaturated acids readily lose carbon dioxide

and hydrogen bromide to give brominated hydrocarbons :—

$$R.CHBr.CHBr.COOH \rightarrow R.CH:CHBr.$$

Methylcyclohexylideneacetic acid behaves in a similar way (Marckwald and Meth, *Ber.*, 1906, xxxix., 2404), for when treated with bromine in aqueous sodium carbonate solution it is converted into 1-methyl-4-bromomethylene-hexahydrobenzene, which on heating with water forms

$$CH_3.CH<\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}>C=CHBr.$$

hexahydro-*p*-tolualdehyde. Perkin and Pope (*Proc. Chem. Soc.*, xxii., 107) prepared their methylcyclohexylidene-acetic acid by eliminating the elements of hydrogen bromide from α-bromohexahydro-*p*-tolylacetic acid, and, as

$$CH_3.CH<\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}>CH—CHBr—COOH.$$

shown by Ruppe, Roners, and Lotz (*Ber.*, 1902, xxxv., 265), both α*β*- and *β*γ-unsaturated acids are formed by loss of hydrogen bromide from α-bromo acids. Marckwald and Meth suggest that Perkin and Pope's acid is 1-methyl-Δ^3-tetrahydrobenzeneacetic acid, and that the methylcyclo-

$$CH_2.CH<\begin{matrix}CH_2—CH\\CH_2—CH_2\end{matrix}>C.CH_2.COOH.$$

hexylideneacetic acid, which would be produced at the same time, was overlooked on account of its extreme solubility in all organic solvents.

m-Hydroxybenzoic acid can be readily reduced by sodium and alcohol (Perkin and Tattersall, *Journ. Chem. Soc.*, 1907, xci., 480) to form cyclohexanol-3-carboxylic

$$CH_2<\begin{matrix}CHOH—CH_2\\CH_2——CH_2\end{matrix}>CH.COOH.$$

acid, which exists in well-defined *cis*- and *trans*-modifications. When oxidised with chromic acid it is converted into cyclohexanone-3-carboxylic acid, the ethyl salt of which has been used as the starting-point in the synthetical preparation of carvestrene. The method of preparing *ε*-ketohexahydrobenzoic acid from pentane-αγε-tricarboxylic acid is very laborious, and a decided improvement has now been introduced (Kay and Perkin, *Ibid.*, 1906, lxxxix., 1640) by heating the ethyl ester of the above acid with sodium, when ethyl cyclohexanone-2 : 4-dicarboxylate is formed, which, when digested with dilute

$$C_2H_5OOC.CH<\begin{matrix}CH_2.CH_2.COOC_2H_5\\CH_2.CH_2.COOC_2H_5\end{matrix}\rightarrow$$

$$\rightarrow C_2H_5.OOC.CH<\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}>CO.COOC_2H_5$$

sulphuric acid, is readily decomposed with formation of *ε*-ketohexahydrobenzoic acid, carbon dioxide, and ethyl alcohol.

Confirmation of the formulæ assigned by Baeyer (*Annalen*, 1892, cclxix., 145) to the different forms of dihydrophthalic acids has been furnished through the resolution of *trans*-$\Delta^{3:5}$-dihydrophthalic acid (Neville, *Journ. Chem. Soc.*, 1906, lxxxix., 1744) into two active isomerides by crystallising the strychnine hydrogen salt, the isomerides having $[\alpha]_D$ 126°. Baeyer stated that when treated with caustic soda the *trans*-$\Delta^{3:5}$ acid was converted into the $\Delta^{2:6}$ variety ; and with acetic anhydride it passed the *cis* $\Delta^{3:5}$ modification. As neither of these forms contains an asymmetric carbon atom the optical activity ought to be destroyed by treatment with these reagents. This takes place in both cases, the change from one modification to the other proving to be a unimolecular reaction under the conditions of experiment.

A comparison of the electrical conductivities of α- and *β*-naphthoic, benzoic, and phthalic acids with their hydrogenised derivatives leads Abati (*Cent. Blatt.*, 1907, i., 886) to the conclusion that, apart from the strongly negative character of the aromatic nucleus, the presence and position of double bonds in these acids has an undoubted influence on their conductivities, which is increased by a double bond in the αα- or *β*γ-positions, whereas if in the α*β*- or γ*δ*-positions practically the same value is obtained as for the corresponding saturated acids. The author considers this to be contrary to the declarations of Fichter and Pfister (*Annalen*, 1904, cccxxxiv., 201), and does not consider that constitutional formulæ should be assigned from the results of single reactions, as has been done by Perkin and Pickles (*Journ. Chem. Soc.*, 1905, lxxxvii., 293) in the case of the tetrahydroisophthalic acids. Abati and Minerva (*Cent. Blatt.*, 1907, i., 887) have isolated hydrophthalic acids by the reduction of phthalic acid with sodium amalgam, and give the principal properties of these acids and their anhydrides.

Steric Hindrance in the Formation of Rings.—The interaction of the 1 : 4-dibromides and primary aromatic amines has been previously shown by Scholtz (*Ber.*, 1898, xxxi., 414, 627, 1154, 1707 ; and 1899, xxxii., 848) to take place in one or two ways, according as to whether the primary amine contains a substituting group in the ortho-position or not. Thus, with *o*-xylylene dibromide and aniline or *m*- and *p*-toluidine a five-ring compound is formed :—

$$C_6H_4<\begin{matrix}CH_2Br\\CH_2Br\end{matrix}+H_2N.C_6H_5=$$

$$=C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>N.C_6H_5+2HBr ;$$

whereas when *o*-toluidine is used an open chain substance results :—

$$C_6H_4<\begin{matrix}CH_2Br\\CH_2Br\end{matrix}+2H_2N.C_6H_4.CH_3=$$

$$=C_6H_4<\begin{matrix}CH_2.NH.C_6H_4.CH_3\\CH_2.NH.C_6H_4.CH_3\end{matrix}+2HBr.$$

The reaction has now been extended to the formation of six-ring systems (Scholtz, *Ber.*, 1907, xl., 852), where the condensation of numerous substances has shown that exactly similar conditions hold good ; for *o*-toluidine condenses with pentamethylene dibromide to give pentamethylene-di-*o*-toluidine, $(CH_2)_5.(NH.C_6H_4.CH_3)_2$, whereas with *m*- or *p*-toluidine there is formed *m*- or *p*-tolylpiperidine.

$$CH_2<\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}>N.C_6H_4.CH_3.$$

Optical Influence of Conjugated Unsaturated Groups.—Kay and Perkin (*Journ. Chem. Soc.*, 1906, lxxxix., 839) have shown that the magnetic rotation of *d*-limonene differs from that of $\Delta^{3,8(9)}$-*p*-menthadiene, of which the value is abnormally high, and they expressed the belief that this was due to the presence of two conjugated double bonds. Bruhl (*Journ. Chem. Soc.*, 1907, xci., 115 ; see also *Ber.*, 1907, xl., 878) points out that this is correct, and that the high value could have been predicted with certainty, for Bruhl's previous work has proved that the numbers for the magnetic rotations and refractive values of substances are always largely increased by the presence of conjugated double linkings, not only C:C.C:C but also C:C.C:O. Only benzene derivatives, which contain monovalent atoms or groups substituting hydrogen atoms of the ring, give normal values, and here it is presumed that the three double bonds mutually neutralise one another. As soon as the symmetry of the six carbon atoms is disturbed by the introduction of CH_2 between the members of the ring, or by coupling the ring with other unsaturated groups, such as C:C, C:O, NO_2, &c., then the characteristic increase in value due to the conjugated bonds is shown.

Velocity of Chemical Change in the Polymethylene Series.—The following may be quoted as some of the more important general results of the study of polymethylene derivatives in respect to the velocity of chemical change (Menschutkin, *Journ. Chem. Soc.*, 1906, lxxxix., 1532).

The formation of the closed polymethylene ring from an open chain of normal structure proceeds with increase of velocity, the maximum occurring in the formation of

the pentamethylene ring, decreasing through the hexamethylene, to the minimum increase in the case of the heptamethylene ring. The increase of velocity at the closing of the open chain is not a specific property of the polymethylene ring, but is observed in the formation of all rings, alicyclic and heterocyclic. The secondary polymethylene alcohols, in which the hydroxyl group is attached to the carbon atom of the ring, are typical secondary alcohols. Their esterification constants are higher than those of the normal saturated secondary alcohols; derivatives of cyclopentanol giving the highest, cyclohexanol much lower, and cycloheptanol the lowest values. The esterification constants of polymethylene tertiary alcohols are very low, but esterification proceeds regularly. This is characteristic of phenols, and does not occur with saturated tertiary alcohols. When side chains are present in the ortho- or diortho-positions a great decrease in the esterification constants is observed, an effect commonly ascribed to the benzene ring alone, but in reality a general property of all chains. Side chains in positions 3 or 4 of the polymethylene series produce an increase of the constants; and as open chain compounds show no such increase of velocity this provides an important characteristic of closed chains. When a hexamethylene ring is introduced into the open chain of an alcohol the decrease of the esterification constants is much larger than is effected by the benzene ring.

ON THE NATURE OF VALENCY.*

By Prof. W. J. POPE and W. BARLOW.

(Concluded from p. 82).

FROM the cases here briefly described, which with others have been discussed in detail elsewhere (*Trans. Chem. Soc.*, 1907, xci., 1150), it is concluded that the crystal structures of compounds composed of two or more elements of the same valency are to be regarded as close-packed homogeneous assemblages of spheres; atoms of the different component elements are to be represented in the assemblage by different kinds of spheres, and all are nearly, but not precisely, of the same volume. The assemblage of spheres is to be regarded as subject to pressure for the purpose of eliminating interstitial space, and so causing the assemblage to simulate an equilibrium between centres of attraction and repulsion. An indication is thus obtained that in the substances concerned the volume appropriated by each atom is approximately proportional to its valency; it is also clear that crystalline substances are, in general, capable of formulation as close-packed assemblages of spheres, each of which represents the sphere of influence of a component atom. On considering the properties of close-packed homogeneous assemblages of spheres of different sizes, the assemblages being supposed subject to the previously mentioned condition as to compression, two are found which are of special importance. These are termed the first and second geometrical properties of homogeneous close-packed assemblages of spheres, and may be stated in the following terms:—

First Geometrical Property. Let homogeneously situated spheres, each of volume m, be removed from a homogeneous, close-packed assemblage of deformable spheres, and let the similar vacant spaces disclosed be reoccupied each by a similar group consisting of two or more spheres having the total volume m: then if the shape of the cavities can, without re-marshalling the assemblage, be adjusted to the shape of the introduced groups by some mere distortion and local adjustment, the close-packing is found to be preserved.

Second Geometrical Property.—If the molecular units of two homogeneous assemblages of deformable spheres, which are about equally closely packed, are partially similar in composition, and the similar parts have the same marshalling in both, whilst the dissimilar parts are of different valency volumes, the amount of the difference will be two volumes, or a simple multiple, 2, 3, or 4, of two volumes of the sphere of influence of minimum magnitude, namely, corresponding to valency 1, for every molecular unit.

The first geometrical property is entirely analogous to that aspect of the doctrine of valency which says that one set of atoms of the total valency m is chemically replaceable by another set of atoms of the total valency m. The second geometrical property is entirely analogous to that aspect of chemical substitution which states that if an atom of valency m is replaced by one of valency $m+n$, other atoms of the total valency n must also be introduced in order that the type of the original molecular structure may be preserved; it also shows why a multivalent element in general changes its valency by 2 or by integral multiples of 2 units. This close analogy between the indications of the doctrine of valency and the properties of close-packed assemblages of spheres is put forward as having a physical meaning, and leads to the conclusion that in a crystalline substance each component atom appropriates a portion of space which is approximately proportional in volume to its fundamental valency. The fundamental valency of an element must thus be regarded as of a different nature from other valencies exhibited by the same element, just as has been indicated by the work of Werner and Abegg, and it has not thus far been found necessary to suppose that multivalent elements affect, under different conditions of combination, spheres of influence of different sizes corresponding to the several valencies. The sphere of influence of nitrogen is of approximately three times the volume of that of hydrogen both in ammonia and ammonium chloride, and that of sulphur is approximately twice as large as that of hydrogen in compounds in which this element is di-, tetra-, or hexavalent.

It should be observed that the relation noted between the volumes of the spheres of influence and the valencies of the element is to be expected to hold in all compounds, each taken alone, but that it does not necessarily hold as between one compound and another, or between different physical states of any one compound. As above indicated, the relative and not the absolute volumes are alone concerned in the present work. If the above view of the nature of crystalline substances is correct, each crystalline substance must be regarded as a close-packed homogeneous assemblage of the spheres of atomic influence, and the chemical molecule must be regarded as the contents of the cell produced by an appropriate homogeneous geometrical partitioning of the assemblage into clusters of spheres. Much evidence of the correctness of this mode of formulation has been quoted above and more may be now conveniently given.

If, in a series of related substances, the axial ratios are so chosen, either by accident or design, as to refer to the relative dimensions of similar parts of the crystal structure in the several cases, the equivalence parameters should at once reveal the relation between the substances. This is seen in the case of the humite group of minerals, which consists of the monosymmetric chondrodite, $Mg_3(SiO_4)_2.2Mg(F,OH)$; the orthorhombic humite, $Mg_5(SiO_4)_3.2Mg(F,OH)$; and the monosymmetric clinohumite, $Mg_7(SiO_4)_4.2Mg(F,OH)$; the axial ratios and equivalence parameters of these substances are given in Table A. The practical constancy of the values x, y, and z/W (W being the sum of the valencies or the valency volume) indicates that the increment of the series, Mg_2SiO_4, is introduced as a succession of layers which lie parallel to the directions a and b and perpendicular to the direction c. The increment of composition in the series is Mg_2SiO_4, the composition of the orthorhombic forsterite, and by subtracting the increment from the composition of chondrodite the residue, $MgSiO_4.2Mg(F,OH)$,

* Paper forming the basis of a Discussion on this subject at the Leicester Meeting of the British Association (Section B), 1907.

Table A.

		W.	*a* : *b* : *c*	*x* : *y* : *z*	z/W.
Chondrodite		38	1·08830 : 1 : 3·14472	2·4249 : 2·2323 : 7·0199	0·18473
Humite		54	1·08021 : 1 : 4·49334	2·4278 : 2·2475 : 9·8965	0·18327
Clinohumite		70	1·08028 : 1 : 5·65883	2·4349 : 2·2540 : 12·7547	0·18221
Prolectite	Observed ..	22	1·0803 : 1 : 1·8862	2·3877 : 2·2102 : 4·1689	
	Calculated ..		1·0822 : 1 : 1·8500	2·4292 : 2·2446 : 4·1526	
Forsterite	Observed ..	16	0·9296 : 1 : 1·1714	2·4492 : 2·2769 : 2·8691	
	Calculated ..		0·9240 : 1 : 1·1804	2·4292 : 2·2446 : 2·8674	

Table B.

d-$C_{10}H_{14}O_4$	60	1·0011 : 1 : 1·7270	3·2655 : 3·2618 : 5·6331	
d-$C_{10}H_{16}O_4$,$\frac{1}{2}(CH_3)_2CO$ ..	74	1·2386 : 1 : 1·7172	4·0435 : 3·2646 : 5·6060	

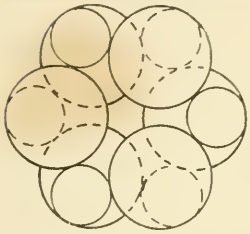


Fig. 6*a*.

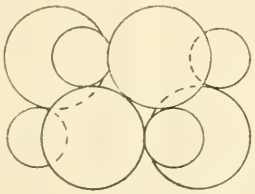


Fig. 6*b*.

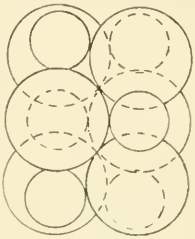


Fig. 6*c*.

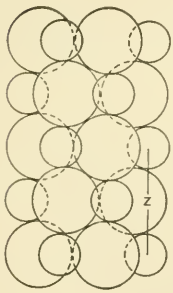


Fig. 7.

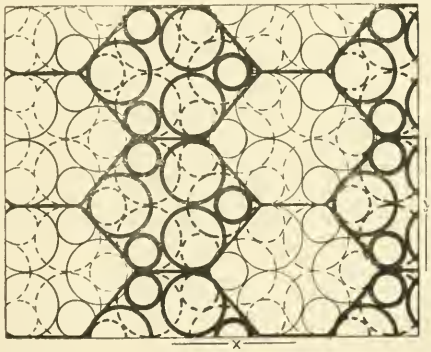


Fig. 8.

is obtained; this is the composition attributed to the monosymmetric prolectite. The equivalence parameters and the axial ratios for the two last-named minerals should be deducible from the data given for the first three; the values thus calculated and those actually observed are given in Table A.

The dimensions of the increment layer agree closely with those of the mineral forsterite, and a similar close agreement is found between the calculated and observed dimensions of the layer which may be regarded as the foundation of the series and has the composition of prolectite.

Another interesting case of similar character is furnished by the comparison of the two orthorhombic compounds, *d*-camphoric anhydride and the addition compound of *d*-camphoric acid with acetone, data for which are given in Table B.

The fact that the passage from the simpler to the more complex compound is accompanied by an increase of one of the three equivalence parameters, whilst the other two remain practically unchanged, is again indicative of the relation which the analogy suggests as existing between the relative molecular dimensions and the valency of the constituent atoms.

The first geometrical property would appear to be responsible for the close morphotropic relationships observed between the members of each of the following pairs of substances:—

1. Ammonium iodate and ammonium fluoriodate, NH_4IO_3 and $NH_4IF_2O_3$.
2. The stable and labile *o*-sulphobenzoic chlorides,—

$$C_6H_4\begin{matrix}SO_2Cl\\COCl\end{matrix} \text{ and } C_6H_4\begin{matrix}SO_2\\CCl_2\end{matrix}>O.$$

3. Phthalic and *o*-sulphobenzoic acid,—

$$C_6H_4(CO.OH)_2 \text{ and } C_6H_4{<}^{CO.OH}_{SO_2.OH}.$$

4. Benzoic acid and benzenesulphonic acid, $C_6H_5.CO_2H$ and $C_6H_5.SO_3H$.

5. Sulphoacetic and methionic acids,—

$$CH_2{<}^{CO.OH}_{SO_2.OH} \text{ and } CH_2(SO_2.OH)_2.$$

The second geometrical property may be regarded as responsible for the close crystallographic relationship observed between the rhombohedral sodium nitrate and calcite, the orthorhombic potassium nitrate and aragonite, the alkali salts of methanedisulphonic acid, $CH_2(SO_3H)_2$, and iminodisulphonic acid, $NH(SO_3H)_2$, and between benzene, aniline hydrobromide, and aniline nitrate (*Trans. Chem. Soc.*, 1906, 1732).

Since the publication of the conclusions here described as to the nature of valency important corroborative evidence has been put forward by Le Bas (*Trans. Chem. Soc.*, 1907, 112) and by Traube (*Berichte*, 1907, xl., 130, 723). Le Bas shows that the molecular volumes of the normal paraffinoid hydrocarbons determined in the liquid state at the melting point, and hence under practically corresponding conditions, can be calculated with great accuracy as the product of the sum of the valencies, or the valency volume W, and a unit stere S, having the value 2·970. The latter value represents the volume appropriated by a hydrogen atom in each of the liquid substances, and is one-fourth of the volume appropriated by a carbon atom throughout the series of compounds. The kind of correspondence which holds between the observed and calculated values is conveniently illustrated by the following table, given by Le Bas:—

Saturated Normal Paraffins.

	W.	Mol. vol. =V.	M.p./b.p.	V/W=S.	W×S= calculated mol. vol.
$C_{11}H_{24}$ ..	68	201·4	0·527	2·962	201·96
$C_{12}H_{26}$ ..	74	219·9	0·536	2·971	219·78
$C_{13}H_{28}$ ..	80	237·3	0·524	2·966	237·60
$C_{14}H_{30}$ ..	86	255·4	0·530	2·970	255·42
$C_{15}H_{32}$ ..	92	273·2	0·520	2·970	273·24
$C_{16}H_{34}$ ..	98	291·2	0·519	2·971	291·06
$C_{17}H_{36}$ ..	104	309·0	0·513	2·971	308·88
$C_{18}H_{38}$ ..	110	326·9	0·512	2·971	326·70
$C_{19}H_{40}$ ..	116	344·7	0·506	2·971	344·52
$C_{20}H_{42}$ ..	122	362·5		2·971	362·34
$C_{21}H_{44}$ ..	128	380·3		2·971	380·16
$C_{22}H_{46}$ ..	134	398·3		2·972	398·00
$C_{23}H_{48}$ ..	140	416·2		2·971	415·80
$C_{24}H_{50}$ ..	146	434·1		2·973	433·62
$C_{27}H_{56}$ ..	164	487·4		2·972	487·08
$C_{31}H_{64}$ ..	188	558·4		2·970	558·36
$C_{32}H_{66}$ ..	194	576·2		2·970	576·18
$C_{35}H_{72}$ ..	212	629·5		2·969	629·64

Mean value of S = 2·970.

Similar results have been obtained by Traube with molecular volumes and molecular refractions; they indicate that in the particular cases discussed the spheres of influence of the component elements remain of the same volumes throughout the series under corresponding conditions. Barlow and Pope indicated that the spheres of influence are approximately proportional in volume to the valencies in one and the same compound, and did not suggest that in general the sphere of influence of a particular element would preserve its volume on passing from compound to compound. It should of course be possible to compare series of substances under temperatures and pressures at which the relation indicated by Le Bas holds, and, in the case of the normal paraffins, it appears that these temperatures are the corresponding temperatures.

Accepting the conclusion that crystalline substances are to be regarded as homogeneous close-packed assemblages of spheres of atomic influence, the latter having volumes approximately proportional to the valencies of the corresponding elements, it is possible to deduce configurations for organic substances of considerable molecular complexity. Applying the method described above to the case of benzene, with the aid of the known crystalline form and the chemical properties of the hydrocarbon, an assemblage representing benzene can be derived, and this, by appropriate geometrical partitioning, can be divided into cells each containing one chemical molecule. The molecular configuration of benzene thus derived is shown in plan and two elevations in Fig. 6, *a*, *b*, and *c*; these molecular groups are arranged in columns as shown in Fig. 7, and these columns are packed in the crystalline assemblage in the manner indicated in plan in Fig. 8. In the assemblage the columns are arranged in walls, and the latter are packed together on two different levels, as shown by the lightly and heavily marked circles in Fig. 8. The nature of the partitioning which divides the assemblage into cells each containing one complex, C_6H_6, is indicated by the heavily marked hexagonal outlines shown in the diagram. The equivalence parameters, $x : y : z = 3·101 : 3·480 : 2·780$, calculated from the axial ratios, $a : b : c = 0·891 : 1 : 0·799$, of the orthorhombic crystalline hydrocarbon are indicated in the diagrams. The configuration thus derived represents the facts involved in the isomerism of, and the absence of enantiomorphism in, benzene derivatives; it also indicates a difference in kind between the meta-position as compared with the ortho- and para- positions (*Trans. Chem. Soc.*, 1906, 1692).

In addition to the results briefly described in the foregoing pages and which have already been published, it has been found that assemblages representative of all the paraffins, the olefines, and acetylenic hydrocarbons can be devised, and that these exhibit properties corresponding to those of the various substances. It has also been found that in the cases of tautomeric substances alternative methods of partitioning the assemblage are possible, and that these different modes of partitioning lead to the production of molecular units corresponding in constitution to the several tautomeric or dynamically isomeric modifications.

AN ELECTRICAL EXPERIMENT FOR ILLUSTRATING THE TWO MODES OF CONDENSATION OF MOISTURE ON SOLID SURFACES.

By Prof. FRED. T. TROUTON, F.R.S.

EXPERIMENT has shown what might perhaps have been anticipated from theoretical considerations, that there are two possible modes in which condensed water vapour on solid surfaces can exist and be in equilibrium with a given vapour pressure.

After which of these modes condensation will take place on bringing a surface into a moist atmosphere depends on its previous history. If the surface has been dried at a high temperature with the aid of phosphorus pentoxide the amount of moisture is relatively small, and is said to be of the *a* type, but if the drying has been effected at only ordinary temperatures there is considerably greater condensation, called the *b* type. This is attributed to there being in the latter case still some of the liquid on the surface, affording an example or nucleus for liquid condensation of the *b* type; while in the former case the condensation is more analogous to the supersaturated state which can occur when a vapour is compressed along an isothermal in the absence of the nuclei necessary for condensation.

When a completely dried surface of glass is placed in an atmosphere of which the moisture is gradually increased

* A Paper read before the British Association (Section A), Leicester Meeting, 1907.

up from zero, the course of events is as follows :—At first very little moisture condenses compared to that which takes place if the drying has been incomplete, but on reaching a certain critical vapour pressure the condensation is very rapid, and is now of the *b* type.

The electrical conductivity of these two types of condensed surface layers is very different. A comparative experiment was made in which two rods of glass were laid from earth to the knobs of two electroscopes passed up for the purpose into a vessel in which the percentage of moisture could be changed at will. One of these rods was dried by heating, while the other was not. As the percentage of moisture was increased, the air-dried rod was observed to gradually acquire considerable conducting powers, but the other rod did not conduct until the critical pressure was reached, when it did so suddenly. The critical pressure for glass is roughly 50 per cent saturation, the same as that found by the deposition method described above.

In the case of shellac the critical pressure was found to be above 90 per cent. A simple experiment illustrating the two modes of condensation was exhibited. An electroscope with shellac insulation was covered by a bell-jar which had previously been held for a moment over a Bunsen flame, so as to acquire a damp atmosphere. No discharge occurred. The experiment was now repeated, but the shellac was first moistened, and then dried with a cloth so as to again insulate. On the electroscope being covered by the bell-jar immediate discharge took place, even though, in the meantime, the air in the jar must have somewhat dried; this was of the *b* or conducting type of condensation.

On now melting the surface of the shellac so as to completely dry it, the surface was found to have reverted to the condition in which the *a* type of condensation is deposited.

THE ABSORPTION OF GASES BY CHARCOAL.*

By Miss IDA F. HOMFRAY.

The experiments of which an account is here submitted were devised, at the suggestion of Sir William Ramsay, to throw some light on the question of the absorption of gases in charcoal. The gas which appeared most suitable for the purpose, on account of its molecular simplicity and chemical inertness, was argon. The apparatus used was similar to a constant-volume gas thermometer, the bulb containing 3 grms. of charcoal. This was connected with a gas burette, a gas reservoir, and a Sprengel pump, all connections being of glass and sealed.

Various constant temperature baths were used, ranging from boiling water to liquid-air temperatures, and successive quantities of argon were admitted from the burette, the pressures being read at each temperature. Isothermal curves were then plotted, taking pressures as ordinates and concentrations (corrected for dead space and reduced to standard conditions) as abscissæ. From these curves points of equal concentration were read off and a fresh series of curves were obtained, having pressures as ordinates and absolute temperatures as abscissæ. Such curves have been termed by Ostwald "isosteres." Each curve corresponds thus to a vapour-pressure curve in the univariant system of a vapour in contact with its own liquid, and is analogous to it in form.

Ramsay and Young's law for the ratios of the absolute temperatures of two vapours at the same pressure was then applied to these results in the form :—

$$\frac{T_0}{T_1} - \frac{T_0'}{T_1'} = K(T_0 - T_0');$$

where T_1 T_1' are the absolute temperatures read from one of the isosteric curves corresponding to any two pressures, and T_0 T_0' the absolute temperatures of any other vapour, taken as standard, at the same two pressures. Water, oxygen, and argon were successively taken as standards, and the equation was found to hold in all cases. A series of straight lines, one for each concentration, was thus obtained.

It has been shown by Professor Porter that Ramsay and Young's law may be directly derived from Bertrand's vapour-pressure formula,—

$$P = G\left(\frac{T - a}{T}\right)^n,$$

provided that the constant n is the same for all vapours. For a large range of vapours it is found that if $n = 50$ very good correspondence is obtained. This was found also to be the case with the results of the present experiments.

Values of the other constants a and g were calculated for each concentration as well as for argon vapour itself.

An attempt has been made to correlate these constants with numbers representing the actual concentrations, and, in order to introduce the argon-vapour constants at a finite concentration, the concentrations were calculated in terms of weight of argon in 100 grms. of the mixture—a method frequently used in the case of solutions. The concentrations experimentally reached varied from 0·317 to 7·089 per cent, the vapour in the absence of charcoal being represented by 100 per cent.

For convenience the logarithms of the concentrations were plotted against values of a and G respectively, and a smooth curve was obtained terminating at 100 per cent in the constants for argon.

Equations were then obtained which express with considerable accuracy these curves, and when introduced into Bertrand's equation, the corresponding temperatures or pressures calculated for any concentration are in very fair agreement with those experimentally found, except for exceedingly small concentrations.

These equations are—

$$a = 13{\cdot}12 + \frac{250}{24}\left\{\log \frac{100}{C}\right\}$$

$$\log g = 0{\cdot}1085 - 0{\cdot}012\left\{\log \frac{100}{C+1}\right\}$$

where $g = (G)^{\frac{1}{50}}$.

The values 13·12 and 0·1085 are the values respectively of a and log g for argon vapour. The equations given in this paper are in much better agreement with observation than the logarithmic or exponential equations usually employed to express the isotherms.

* A Paper read before the British Association (Section A), Leicester Meeting, 1907.

Structural Stability of Ethylene Oxide. — Louis Henry.—Grignard states that the reaction of the organo-magnesium compounds on ethylene oxide, $\overset{CH_2—CH_2}{\diagdown O \diagup}$, gives rise to primary alcohols, but the author considered that this statement was open to doubt, because ethylene iodo-hydrine, $(HO)CH_2—CH_2I$, with organo-zinc compounds gives secondary alcohols, and, moreover, isobutylene oxide with magnesium methyl bromide gives secondary isoamyl alcohol, $(CH_3)_2=CH.CH(OH)—CH_3$. Since isobutylene oxide reacts in the same way as its isomer isobutyric aldehyde with magnesium methyl bromide, and since ethyl glycol, $(HO)CH_2—CH_2(OH)$, gives acetic aldehyde, $CH_3—CH=O$, under the same conditions as isobutyl glycol gives isobutyric aldehyde, it was to be expected that ethylene oxide (of which isobutylene oxide is the dimethyl derivative) would give rise to the aldehyde $CH_3—CH=O$, *i.e.*; to secondary alcohols. But secondary alcohols are not formed, and thus ethylene oxide does not behave like its dimethyl derivative. This fact is a remarkable example of the stability which excess of hydrogen communicates to residues and molecules containing carbon; thus hydrogen may be regarded as the cementing factor.—*Comptes Rendus*, cxlv., No. 3.

THE CONSTITUTION OF THE ATOM.*

Discussion.

The debate was opened by Prof. E. Rutherford, F.R.S., who gave a brief historical sketch of existing knowledge regarding the constitution of the atom. He said that the fundamental idea dated from the time of Dalton, but that at the present day the chemist did not regard the atom as the smallest possible particle of matter. For the last ten years physical researches had afforded experimental proofs of the atomic theory, and so far as it existed as a working chemical theory recent knowledge had not undermined it but had materially strengthened it. Coming down to purely physical work, he said that the electron must be looked upon as a sphere of electricity or as an electrified sphere. Its diameter was known to be of the order of 10^{-13} cm., and its sphere of action 10^{-12} cm. He was sure that the electron had come to stay, and that it was a constituent of all matter. Nevertheless, the stability of the atom of matter was not affected by the liberation of one or more electrons. He then referred to Lord Kelvin's idea of a number of electrons being contained by a sphere of positive electrification, and to Prof. J. J. Thomson's idea of a similar arrangement, practically the only difference being that Thomson's electrons were revolving in rings, whereas Kelvin's were stationary. He was convinced that hydrogen played a most important part in electrical conduction, and dealt further with the question of an electron being tacked on to each hydrogen atom. So far as he himself was concerned, he believed in the existence of a positive electron, and he described briefly the work of a German *savant* who claimed to have discovered positive electrons. He thought it had not been isolated hitherto simply because everybody expected that it would have properties exactly opposite to those of the negative electron, or, in other words, that it would be the mirror image of the negative electron. It might, on the contrary, have entirely different properties, and so elude the vigilance of those who were seeking it. With regard to spectrum analysis, he was of the opinion that it would not be of very great use in the investigation of the constitution of the atom. The spectrum of an element was probably not due to the element at all, but to the superficially attached electrons. Thus it might happen—and he inclined to the opinion that it did—that the spectrum due to the internal electrons of an atom—*i.e.*, to the element itself—existed only in the ultra-violet part of the spectrum and had never yet been observed. This would account for the variation of the so-called spectrum of an element with temperature. There was evidence for the radio-active point of view which showed that electrons in atoms were in violent motion, as otherwise they could not be expelled with the velocity of light.

The next speaker in the discussion was Sir Oliver Lodge, who at once avowed himself as the champion of the electric theory of matter. At all events he claimed that it was a splendid working hypothesis. He knew that everybody was not of this opinion, and Lord Kelvin himself did not hold it. In this connection he recognised that it was hazardous and interesting—painfully interesting—to differ from Lord Kelvin. He maintained the electric theory, because in whatever direction it was applied it did not break down, and if it did not break down, then it was good enough until something better turned up. The inertia of matter, for instance, could be explained electrically, because when an electric charge was in motion it set up an electric field, and an exercise of force was required to stop or retard it. Radiation could also be explained, for, when an electric charge was accelerated, it radiated in the proper direction—that is to say, it imparted vibrations to the surrounding ether. With regard to instability, if the atom were considered as a revolving assemblage, then the corpuscles experienced a centripedal acceleration and radiated, whence instability was set up. He agreed with Prof. Rutherford that the difficulty of the whole matter lay in the positive charge, of the existence of which there was no evidence whatever.

Sir Wm. Ramsay, who rose next, said that from the chemist's point of view the interest lay in the satellites or detachable electrons, and not in the internal or constitutional electrons of the atoms. Hydrogen was not an element at all, but a compound of hydrogen and electrons. Chemists wrote H – to represent an atom of hydrogen, and H – H to represent a molecule, but he was not sure whether they ought not to write H – – H. In the same way, having regard to the electrons present, an atom of what was called hydrogen ought to be written H E, where E stood for an electron. When, however, they considered a molecule of so-called hydrogen, the question arose as to whether they should write it H E H E or H E E H. For himself, he thought the former way was correct. With regard to Prof. Rutherford's statement that loss of electrons had no effect upon an element, he would like to state that, although that might be true, he had distinct evidence that increase of electrons made a difference. For instance, some time ago he sealed up some radium in a glass bulb through which only the β-rays, or electrons, could pass. In proximity to this bulb he placed a number of elements, among which was nickel. This nickel, after being bombarded with electrons, proved to be coated with a radio-active skin, and precipitated as strongly radio-active substance in sulphuric acid.

Mr. F. Soddy expressed the opinion that the time had not yet come to believe in the electric theory of matter. Indeed, all the results of the last twenty-five years of research could be accepted without applying the electric theory of the constitution of matter. He ventured to say that none of the actual experimental results arrived at by chemists concerning this subject had been predicted by physicists. The "predictions" had been applied after the experimental results had been obtained. He could not accept the theory that the loss of energy by an atom produced a change in the matter of which that atom was constituted; at all events, this drain of energy produced no effect such as might be observed by chemists. He was convinced that the ultimate solution of these problems would come from the chemists.

Mr. G. A. Schott said that the new hypothesis of each hydrogen atom having only one electron was unworkable. On this basis there were not sufficient surface electrons to the atom to account for the number of lines in the spectrum of iron, for instance.

Prof. J. Larmor called attention to the fact that radio-activity was not the only cause leading to discussion in these matters, It merely constituted a new group of facts fitting into an old theory. Faraday was really the founder of the electron theory, and he enunciated it when he stated that the separation of matter was proportional to the separation of electricity. Clerk Maxwell, too, wanted to postulate electrons, but they would not fit into his scheme. He (Prof. Larmor) then referred to the beautiful bell analogy of the atom, and said that everything depended on whether the bell was hung on to something else, or whether it was really the atom itself.

Lord Kelvin could not believe that the mere motion of electrons gave the widely different properties and degrees of stability which we knew belonged to different kinds of matter. Nor could he believe that radio-activity was a mere residue of the kinetic energy of the atom, for if so, how could an electron be thrown off with the velocity of light? He preferred rather to regard the atom as a big gun loaded with a shell which again contained a charge, for when the electron was thrown off it did not cause the bursting asunder of the atom any more than the firing of the gun effected its destruction. The electron itself, however, did change its original nature, in exactly the same way as the shell broke into pieces when it exploded.

* For the Report of this Discussion and of the two Papers which follow, read before the British Association (Section A), Leicester Meeting, we are indebted to the courtesy of the Editor of the *Electrician*.

His gun had probably been loaded before there were sun, stars, or any of the things that we now know, and it only required contact with matter to release the trigger and fire off the shell.

Prof. RUTHERFORD replied very briefly.

ON THE VARIABILITY IN THE PRODUCTS RESULTING FROM CHANGES IN RADIUM EMANATION.

By Sir WILLIAM RAMSAY, F.R.S.

THE author commenced by reminding his audience that radium, actinium, and thorium all yield helium, and then proceeded to describe the results of experiments which are nothing short of remarkable. It is known, of course, that the emanation decomposes water with the liberation of excess of hydrogen, but where this excess of hydrogen comes from nobody knows. Sir William Ramsay exposed a solution of copper sulphate to the emanation for about a month, and at the end of that time the residue obtained gave the spectra of both sodium and lithium. The experiments were repeated three times, and the results were perfectly consistent in each case. The presence of sodium was not, of course, surprising, as the containing vessels used were composed of glass, but all the materials were tested for lithium, and there was not a trace before the experiments were commenced. Nevertheless, Sir William Ramsay expressed a doubt as to whether the quantity of sodium found could have all come from the glass, and he is going to undertake further investigations in this direction. His next experiment was with copper nitrate, when lithium was again detected after a solution had been exposed to the emanation. Fresh copper nitrate not so treated with the emanation showed no sign of the presence of lithium. In both cases, however, sodium sulphate was detected, but the treated substance showed just twice as much (1·6 mgrms.) as the untreated substance. On evaporating water treated with the emanation 0·3 mgrm. of solid was obtained, while the inactive gas produced was neon with a trace of helium. Gases from the treated copper nitrate solution contained argon, with possibly a trace of neon. He remarked that 1 cc. of emanation gives off three and a-half million times as much energy as 1 cc. of a mixture of hydrogen and oxygen when exploded, and suggested that some of this vast amount of energy might account for the presence of the elements which he had found.

The Hon. R. J. STRUTT confessed that he could not find any source of error in Sir William Ramsay's experiments to account for the presence of neon in the case of water and emanation. He made a rough calculation in order to determine how much air would be required to provide the amount of neon (0·5 cubic mm.) obtained by Sir William Ramsay, and found that it was about 100 cc. In these circumstances, he was sure that there could not have been such a large leakage of air to the apparatus as would account for this quantity. He further mentioned that there was quite sufficient lithium in quartz vessels to give a very distinct spectrum.

Prof. RUTHERFORD complained that the amount of radium in the possession of experimenters was deplorably small. There were only about two laboratories in the world that were in a position to repeat Ramsay's experiments, and if only an experimenter could have a grm. instead of 100 mgrms. at his disposal there would be a very great deal more work done.

Prof. H. E. ARMSTRONG, F.R.S., put forward the suggestion that the so-called inert gases are in reality very active, and that they are not monatomic at all.

In reply, Sir WILLIAM RAMSAY said that helium, when passed through a bath of liquid hydrogen, gave up a considerable amount of krypton.

THE DENSITY OF ETHER.

By Sir OLIVER LODGE.

THE author pointed out that the theory that an electric charge must possess the equivalent of inertia was clearly established by J. J. Thomson in the *Phil. Mag.* for April, 1881, and that the discovery of masses smaller than atoms was made experimentally by J. J. Thomson, and communicated to Section A at Dover in 1889. The theory that the corpuscles so discovered consisted wholly of electric charges was sustained by many people, and was clinched by the experiments of Kaufmann in 1902. The concentration of the ionic charge, required to give the observed corpuscular inertia could be easily calculated; and, consequently, the size of the electric nucleus, or electron, was known. The old conception that a magnetic field was kinetic had been developed by Kelvin, Heaviside, FitzGerald, Hicks, and Larmor, most of whom had treated it as a flow along magnetic lines; though it might also, perhaps equally well, be regarded as a flow perpendicular to them and along the Poynting vector. The former doctrine was sustained by Larmor, as in accordance with the principle of Least Action, and with the absolutely stationary character of the ether as a whole; the latter view appeared to be more consistent with the theories of J. J. Thomson. A change in motion was well known to be surrounded by a magnetic field; and the energy of the motion could be expressed in terms of the energy of this concomitant field, which again must be accounted as the kinetic energy of etherous flow. Putting these things together, and considering the ether as essentially incompressible—on the strength of the Cavendish electric experiment, the facts of gravitation and the general idea of a connecting continuous medium—the author reckoned that to deal with the ether dynamically it must be treated as having a density of the order of 10^{12} grms. per cc. The existence of transverse waves in the interior of a fluid could only be explained on gyrostatic principles, *i.e.*, by the kinetic or rotational elasticity of Lord Kelvin. And the internal circulatory speed of the intrinsic motion of such a fluid must be comparable with the velocity with which such waves were transmitted. Putting these things together, it followed that the intrinsic or constitutional vortex energy of the ether must be of the order 10^{33} ergs per cc. Thus, every cubic mm. of the universal ether of space must possess the equivalent of a thousand tons, and every part of it must be squirming internally with the velocity of light.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

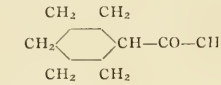
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 3, July 16, 1907.

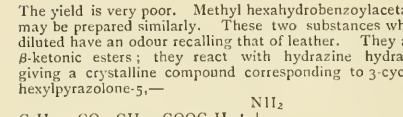
Analysis of Selenium Hexafluoride.—Paul Lebeau.—The gaseous mixture obtained by the action of fluorine upon selenium contains varying quantities of silicon fluoride, which may be eliminated by means of water. The gas can then be liquefied with liquid oxygen and the vapour received into empty flasks. When thus fractionated the gas shows very appreciable differences in density between the first and last fractions. If the gas is heated in a Jena glass vessel a mixture of gases having a volume about one and a-half times that of the original gas is obtained, consisting of silicon fluoride and oxygen. The results of different experiments are not absolutely concordant, and they do not lead to the formula SeF_6. When the gas is heated in tubes of pure silica the quantities of oxygen and silicon fluoride formed are approximately those indicated by the equation

$2SeF_6 + 3SiO_2 = 3SiF_4 + 2SeO_2 + O_2$, but the values found
4 vol. 6 vol. 2 vol.
for oxygen are a little high and for fluorine a little low. To determine the fluorine and silicon in one sample of gas it was decomposed by sodammonium in liquid ammonia. The solution then contained selenide and fluoride of sodium, and a small quantity of selenium is converted into selenite. The selenium of the selenide was precipitated by a current of air, and that of the selenite was determined in the form of sulphide, while the fluorine was separated and weighed as calcium fluoride. The results thus obtained all showed that the gas contains some oxyfluoride, which would be difficult to separate if the boiling-points are not far apart (*cf.* the boiling-points of sulphur hexafluoride and oxyfluoride). The gas in presence of mercury and glass undergoes a purification, and its density rises, which explains the very satisfactory results which Prideaux obtained when he determined its physical constants.

Ethyl Hexahydrobenzoylacetate.—A. Wahl and A. Meyer.—The condensation of dry ethyl hexahydrobenzoate and acetate by means of sodium on a water-bath yields a small quantity of a substance with boiling-point 140—143° under 25 mm. pressure. On analysis this gives the values corresponding to ethyl hexahydrobenzoylacetate :—

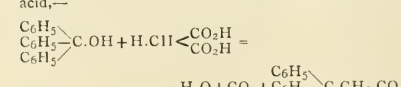


The yield is very poor. Methyl hexahydrobenzoylacetate may be prepared similarly. These two substances when diluted have an odour recalling that of leather. They are β-ketonic esters; they react with hydrazine hydrate, giving a crystalline compound corresponding to 3-cyclohexylpyrazolone-5,—

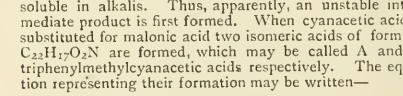


They also give crystalline copper salts with an aqueous solution of copper acetate.

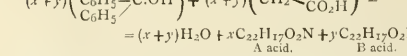
Triphenylcarbinol. Action of Malonic and Cyanacetic Acids.—R. Fosse.—Malonic acid transforms triphenylcarbinol into Henderson's triphenyl-β-propionic acid,—



When the two reagents are heated together an intense red coloration is produced; it fades after a time, and a slightly coloured product remains which is completely soluble in alkalis. Thus, apparently, an unstable intermediate product is first formed. When cyanacetic acid is substituted for malonic acid two isomeric acids of formula $C_{22}H_{17}O_2N$ are formed, which may be called A and B triphenylmethylcyanacetic acids respectively. The equation representing their formation may be written—



When the group CO_2 is removed from these acids the products are two isomers of formula $C_{12}H_{17}N$, which are isomeric with 1.1.1.3-triphenylpropane nitrile obtained from normal triphenylcyanacetic acid,—



Action of Diazochlorides upon γ-Chlorinated Acetoacetic Esters.—G. Favrel.—γ-Chlorinated acetoacetic esters react with diazochlorides giving the 3-hydrazones of the chloro-1-butane dione 2,3-esters. Under the same conditions the α-chlorinated acetoacetic esters give the hydrazones of chlorinated glyoxylic esters, and thus this reaction provides a means of distinguishing between the α- and γ-chlorinated esters.

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2492.

NOTE ON THE USE OF THE RADIOMETER IN OBSERVING SMALL GAS PRESSURES. APPLICATION TO THE DETECTION OF THE GASEOUS PRODUCTS PRODUCED BY RADIO-ACTIVE BODIES.*

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S.

Some time ago I exhibited at a Soirée of the Royal Society a few experiments with the Crookes radiometer, the object being to show that when helium is the residuary gas filling the instrument, an attached charcoal condenser, even when placed in liquid hydrogen, is unable to diminish the pressure by absorption to such an extent that the radiometer will not rotate (when subjected to the concentrated beam of an electric arc lamp focussed upon the black surface of the mica vanes)); while, on the other hand, if the gas instead of being helium is hydrogen, all radiometer motion is suspended. Even when the charcoal condenser of the helium radiometer was cooled in solid hydrogen under exhaustion so that a temperature of 15° absolute was reached, the rotation of the instrument was still very marked. If the radiometer is repeatedly washed out with the mixed oxygen and nitrogen got from the evaporation of liquid air, the charcoal and the whole of the glass being thoroughly heated and the apparatus finally exhausted to a fraction of a millimetre, and sealed off, then, on placing the charcoal tube in liquid air, generally after an hour or two, the vacuum is so high that no motion is induced by the beam of the electric arc. But if instead of liquid air the cooling agent is liquid hydrogen, then two minutes' immersion is sufficient to effect the same result, provided the radiometer is small and the gases get down a quill tube direct into the charcoal. Instead of the gases from liquid air being used to clean out the radiometer as described, it is for some purposes better to seal on a side tube containing perchlorate of potassium, which, when heated, gives pure oxygen. Further, in many experiments, it is advantageous to exhaust the radiometer with its little charcoal condenser by means of a larger quantity of charcoal placed in liquid air for a night, and then to seal the latter off before cooling the special charcoal bulb attached to the radiometer. When a McLeod gauge was sealed on to the end of the bulb containing the charcoal condenser which is cooled in liquid air (no stopcocks of any kind being used), all the mercury vapour was eliminated from the radiometer, and the pressure of the permanent gas was found to be 0·00001 mm., or one seventy-six millionth of an atmosphere. In this condition the radiometer moved when the image of the poles was focussed on the black vanes, and after some fifteen minutes' heating the pressure was found to be only one twenty-five millionth of an atmosphere, and the pressure remained at this after ten hours' cooling of the charcoal condenser in liquid air. The gas produced was no doubt hydrogen, got from the lamp-black of the mica vanes, this being the first time the instrument was used. As a rule, the radiometers require to be re-filled, exhausted, and tested more than once in order to get the motion reduced to a minimum. The importance of the removal of traces of gases like helium, hydrogen, or neon is shown from the fact that a radiometer which has the charcoal removed from the attached bulb, and the latter cooled in liquid hydrogen (the instrument having been previously filled with dry air and exhausted to a fraction of a millimetre of mercury), will not reach such a vacuum as to stop the radiometer motion. Now, as the pressure of nitrogen at the boiling-point of hydrogen must be of the order of a millionth of a millionth of an atmosphere, the action must come either from uncondensable gases, or the persistent adhesion of gas molecules to the glass and vanes of the radiometer, or to some solid matter volatile under the conditions of the experiment. The lowest pressure reached in a charcoal vacuum after ten minutes' cooling in solid hydrogen was still one hundred millionth of an atmosphere. The pressure observed is thus far too high, and it may be that some of this is due to hydrogen coming from the charcoal. To get really high vacua by the charcoal method, even when liquid hydrogen is the cooling agent, it seems necessary to allow the absorption to go on for an hour or more; when the space to be exhausted is relatively large and where narrow tubes or orifices constitute part of the apparatus, as in the McLeod gauge. Further, the presence of any organic matter on the vanes is fatal. No amount of cooling of the charcoal in liquid hydrogen of a radiometer filled as usual and tested in the ordinary manner, in which the vanes were made of pith, make a vacuum sufficient to stop the radiometer motion. The concentrated beam, each time it was applied, was generating gas. In all the experiments the arc used was expending 10 ampères, and the focus was adjusted to about 3 feet from the lamp. The radiometers had a volume of from 150 to 20 cc.

Finding the McLeod gauge very difficult to use, a new method of defining the maximum limit of the working pressure (under the defined circumstances) depending upon the vapour-pressure of mercury was devised. For this purpose a side tube was sealed on to the top of the radiometer, and this, after being bent twice at right angles, ended in a little bulb containing a globule of mercury. After the radiometer and charcoal were heated and exhausted and repeatedly washed out with the gas from liquid air, the charcoal was cooled in liquid air and the mercury allowed to distil for an hour or two. After this treatment, on cooling the mercury with liquid air, the radiometer in a short time became inactive. In this condition the mercury was placed in an alcohol bath at −80° C., and the temperature allowed to rise slowly.

In this way it was found the radiometer action began in the instrument used at −23° C. The pressure of mercury vapour for the temperature derived from the Hertz formulæ is found to be about a fifty millionth of an atmosphere. All the time of the experiment the mercury vapour was being sucked out of the radiometer by the liquid air cooling of the charcoal tube so that the pressure might be less than the saturated pressure. This result at once suggested that the method ought to be applicable to the detection of the gaseous products derived from the transformation of radio-active bodies. In order to test this application, a side tube containing a little radium bromide was sealed on to the bottom of the charcoal condenser, in order to remove the emanation by absorption in the charcoal kept in liquid air. The radiometer, after thorough washing with the gas from liquid air, heating, and exhaustion by a subsidiary charcoal condenser placed in liquid air that was sealed off, was found inactive after the small charcoal receptacle was cooled for an hour in liquid air. The radiometer was again tested after standing fifteen hours, and was found to be quite active. It would seem that the gas produced must be hydrogen, helium, or the alpha particles. In order to eliminate any hydrogen that might be produced, the charcoal condenser of the radiometer was transferred from liquid air, in which it had been kept for some two days, into liquid hydrogen. After half-an-hour's cooling the motion was active when the image of the arc lamp was focussed on the black surface of the mica vanes of the radiometer, and even after one hour's immersion of the charcoal in the liquid hydrogen the motion suffered no diminution. The active gas must therefore have been helium, along with it may be the alpha particles; unless one is being deceived by some solid deposited on the radiometer vanes sufficiently volatile when the arc light is concentrated on them to cause the motion. A similar radio-

* A Paper Read before the Royal Society, June 27, 1907.

meter to that which was used in the radium experiment had a side tube attached containing some 50 grms. of thoria, and after the usual treatment was found inactive. After keeping a fortnight it is now active, but I have not had the opportunity of cooling the charcoal in liquid hydrogen, so that the possibility of the gas being hydrogen has not been eliminated. We might anticipitate that monadic gases of the type of helium and mercury would be more effective than the ordinary gases in inducing radiometer motion. A radiometer with a helium residue will still work under fixed conditions when the gas pressure is four or five times higher than one containing an oxygen residuum. Again, the sensibility of the instrument ought to increase, provided it was subjected to the same intensity of radiation while immersed in liquid air or liquid hydrogen.

The experiments, in any case, seem to show that the radiometer may be used as an efficient instrument of research for the detection of small gas pressures and the study of radio-active products. For quantitative measurements the torsion balance or bifilar suspension must be employed. It would be interesting to repeat light repulsion experiments in the highest attainable charcoal vacuum. Later on I hope to extend the investigation.

THE NATURE OF IONISATION—IONOMANIA.*

By HENRY E. ARMSTRONG.

In his imaginative work on the hypothetical entities termed electrons, in the opening sentence of the chapter which bears the heading "Ionisation of Gases," Sir O. Lodge tells us that "It is constantly necessary to speak of the air being 'ionised' by the passage of rays and many other processes. The term means the molecules are split up or dissociated into their constituent atoms."

The term certainly is used by many in this sense at the present day; yet inadvertently, I venture to contend.

The word "ion" was introduced in 1834 by Faraday in the immortal seventh series of his researches; it was never verbalised by him—I believe advisedly. He was content with "electrolyze." Why should not we be? Faraday coined the words "anion" and "cation," because he felt, he says, that the terms "electro-negative" and "electro-positive" were much too significant for the use to which he would have to put them. His explanation is worthy of notice in these days of uncontrolled speculation and loose reasoning, "for though the meanings are perhaps right, they are only hypothetical, and may be wrong; and then, through a very imperceptible but still very dangerous because continual influence, they do great injury to science by contracting and limiting the habitual views of those engaged in pursuing it." We moderns have no such scruples; our guiding principle seems to be that language is given to us to disguise our thoughts. Every vague conception as it arises must at once be embodied in an ambiguous new word, so that a reader of present-day "scientific" literature often finds himself in a maze of "jargonese." It will be necessary soon to request the Royal Society to maintain a dictionary of terminological inexactitudes as a key to its *Proceedings* and to the publications of scientific bodies.

Surely we have no need to imply more by the term "ionisation" than that the medium is in a state in which it will conduct electricity? We know no more! When a man and his wife have bought Cook's tickets and packed their luggage, they are ionised-ready to travel; but nothing shows them to be divorced. If we have need to introduce the conception of atomic divorce, let us frankly say so and straightforwardly use the word "dissociation." We cannot do better than follow an example set us by Faraday, and, as far as possible, seek to use only such terms as are at the same time "simple in their nature, clear in their reference and from hypothesis." (Footnote, §666, Series 7).

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

I cannot discover, although I have read the Papers many times during the past twenty years for the purpose, that Faraday ever conceived of the ion as a restless wanderer, as a solitary fragment; on the contrary, he appears to have thought of the ion as always accompanied or conducted, and as only delivered up at the boundaries—as separated during electrolysis, *e.g.*:—

§ 665. The chloride of lead is an electrolyte, and when electrolyzed evolves the two ions, chlorine and lead.

§ 827. If one ion be combined in right proporptions with another strongly opposed to it in its ordinary chemical relations, *i.e.*, if an anion be combined with a cation, then both will travel, the one to the anode, the other to the cathode of the decomposing body.

§ 828. If, therefore, an ion pass towards one of the electrodes, another ion must also be passing simultaneously to the other electrode, although, from secondary action, it may not make its appearance.

He distinctly recognised that "attraction of aggregation" lay at the root of electrolytic phenomena—thus he remarks:—

> It is a remarkable circumstance that in gases and vapours, where the attraction of aggregation ceases, there likewise the decomposing powers of electricity apparently cease, and there also the chemical action of quantity is no longer evident. It seems not unlikely that the inability to suffer decomposition in these cases may be dependent upon the absence of that mutual attractive relation of the particles which is the cause of aggregation.

Faraday, in fact, was a pronounced associationist, not a dissociationist. It cannot well be argued that the conception of dissociation was not in his mind; had he foreseen the need of any such explanation he would probably have had little difficulty in formulating it. In his time, chemistry and physics were united sciences and were ionised for joint service, able and willing to co-operate; now they are all but dissociated, and chemistry is cold-shouldered by physics. The consequences of the lack of appreciation and understanding are most unfortunate; I believe really serious. Physicists soar in a mathematical empyrean and have no regard for the plain facts of chemistry. Although they have their being by it and live by it, organic chemistry is tabooed by them. The tangible test-tube has no charms in face of the galvanometer and electrometer; indulgence in speculative lucubrations on the wanderings of a spot of light is too fascinating an occupation.

During the past twenty years I have steadily maintained that the doctrine of electrolytic dissociation is destitute of common-sense. I have discussed the subject on several occasions, and pointed out the inconsistencies, particularly in my Address to the Chemical Society in 1895. I come here to-day, advisedly, to challenge those who accept the creed to reconsider the evidence on which their faith is based. It will not surprise me to be told that faith is something that cannot be based on evidence—merely a longing or desire to believe, felt with special acuteness when facts are inconsiderately in opposition to fancy.

So far as I am aware, the arguments on which the hypothesis is really based are:—(1) The existence of Ohm's law, and (2) the assumption that any electromotive force, however small, will condition sensible electrolysis. Fitzgerald disposed of the first in 1890 (*B.A. Reports*, p. 143; compare my Address, p. 1131) by showing that a modified Grothus hypothesis would fit the facts. As to the second, as it is impossible to avoid some polarisation, the fact cannot be regarded as established. The Helmholtz experiment on which reliance is placed cannot be regarded as irreproachable, it being impossible theoretically to remove a gas entirely from solution by any solvent in contact with the liquid.

Mr. Whetham's thermodynamic missiles have no terrors for me; they are mere bombastic shells. To tell us that,

whatever the process, such and such must be the case, is futile; what we are concerned with is the process. Unless I am altogether mistaken, thermodynamics can tell us nothing of this. Thermodynamic arguments at their best afford but scant comfort to those in search of explanations.

It is the great merit of Arrhenius to have recognised that electrolytic conductivity and chemical activity *se confonde*, as he puts it; that is to say, they are phenomena of the same order. All the conclusions arrived at carry us no further. The dissociation hypothesis was only a way of stating this generalisation; had Arrhenius been a chemist he would never have formulated it, as he would have realised that the hypothesis did not satisfy the postulates generally. At best it was an ingenious paraphase of conventional language in stilted phraseology calculated to mislead the unwary.

Gradually, facts have been accumulated which, I believe, constitute a practically complete refutation of the hypothesis and serve to show that chemical interactions—as Faraday foresaw—are dependent on "mutual attractive relations of the particles," not on dissociation in the sense contended by the Arrhenius-Lodge school. This school assumes that the hydrolytic activity of acids is that of the dissociated hydrogen ions. Hydrolysis can be effected, however, by other agents—in the case of sugars, for example, by enzymes; but the dissociated hydrogen ions should be alike from whatever source they are derived, and it is in accordance with this conclusion that acids may be used without distinction, differing only in the degree of activity which they manifest. Enzymes, however, act selectively; therefore their action cannot be ascribed to dissociated hydrogen ions. Moreover, there is evidence to show that enzymes become associated with the compounds which undergo hydrolysis under their influence; they are not only strictly selective in their action, but are also and only controlled by substances which are of the same configuration as the compounds upon which they act. As there is much evidence that acids can combine with various hydrolytes, there is every reason to suppose that hydrolysis by acids also involves the association of the hydrolyte with the acid.

According to the dissociation hypothesis, the hydrolytic action of an acid should be repressed by salts containing the same anion—the contrary is commonly the case. The increased activity can be accounted for simply and satisfactorily on the assumption that the salt is hydrated in solution, and that hy withdrawing water it raises the concentration of the acid.

Much evidence has been accumulated of late showing that no special distinction is to be drawn between dilute and concentrated solutions and that properties vary continuously throughout all degrees of concentration. The difficulties met with in the past in dealing with concentrated solutions have arisen not only from the existence in them of polymerised molecules, but also from the circumstance that the formation of hydrates has been left out of account; and because solutions have been considered with reference to their volume instead of with reference to the mass of the solvent. The change in the solvent has not been sufficiently considered, and the mistake has been made of assuming that liquids are comparable with gases; a preposterous contention.

It was suggested by Fitzgerald that if the molecules in an electrolyte drew one another apart at a rate proportional to the polarisation, the relation between the electric force and the decomposition would be a linear one, so that Ohm's law would be satisfied. In a forthcoming Paper in the *Proceeding of the Royal Society* on the "Discrimination of Hydrates in Solution," Mr. Caldwell and I have argued that the "ionised" molecules are complex, reversible systems formed of solvent and solute under the influence of the force of residual affinity—*e.g.*,—

$$KCl + OH \rightleftarrows KCl{:}OH_2 \rightleftarrows \overset{H}{\underset{OH}{K\dot{C}l}}.$$

As such systems break down under the influence of the current, new ones to take their place must arise spontaneously in the solution; the molecules therefore would draw one another apart at a rate proportional to the polarisation.

Another point made by Fitzgerald is that:—

> If dissociated atoms are going about in a liquid as in a gas it seems impossible but that they must diffuse at different rates; and that this is not observed seems conclusive evidence against the hypothesis, no matter what else the hypothesis may explain. Consider solution simply. Why does chloride of sodium dissolve in water? There must be some strong affinity between the two of a chemical or semi-chemical nature to break up the cohesion of the crystal; and it seems reasonable to assume that this same affinity keeps the molecules of sodium chloride moving about among the water molecules, so that they diffuse about. Now, if the forces drawing them about be independent of the nature of the molecule, most of the phenomena explained by gaseous laws are explained. Pressure of a gas depends, at any temperature, on the number of molecules and not on their kind. This is Avogadro's law, by which molecular weights are calculated; and if the forces drawing a molecule about in a liquid are independent of the kind of molecule, the very same law of pressure would hold, the pressure forwards of molecules of different kinds would depend on their number only, and, in the same way as Avogadro's law, would enable molecular weights to be calculated.

The forces drawing a molecule about in a liquid are probably of two kinds, if, as I have contended elsewhere, the molecular composition of the solvent be modified in presence of the solute ("The Origin of Osmotic Effects," *Proc. Roy. Soc.*, 1906, A, lxxviii., 264). In a concentrated region the number of solvent monads would be at a maximum, and these would condition a flow of monads from less concentrated regions, which would tend to force out molecules of solute into these latter. In addition, molecules of the solute would be attracted outward by the force which caused it to dissolve—viz., that existent between it and the solvent. To a considerable extent, therefore, the forces drawing a molecule about would be independent of the kind of molecule.

I do not claim Fitzgerald merely as an advocate of views similar to my own. In this section I shall be understood when I say it is because he always seemed to me to be the least biassed and most capable among us of judging in such matters—perhaps the broadest, most generous and sympathetic mind of our generation.

In the July number of the *Philosophical Magazine* it is contended by Sutherland that electrolytes are completely ionised in solution—completely dissociated into ions, that is to say. The grounds on which he arrives at this conclusion are such that if he extend his examination of the problem he will probably find that, although not dissociated into ions, the molecules are all ionised in the sense that they are all prepared to travel in turn—being somewhat in the condition of a crowd of excursionists waiting at a rail way station ready to enter upon their journey as soon as the trains will take them on.

Far too little attention has been paid as yet to such observations as those made by Brereton Baker on the influence of moisture (coupled with acid or alkaline impurity) in conditioning chemical interchanges, and their bearing on the problem of electrical conductivity in gases. The ocular demonstration given recently by Sir James Dewar of the presence of gaseous matter capable of determining the rotation of the radiometer at exhaustions considerably below those at which the conduction of electricity ceases should once more direct attention to the possible need of referring electrical conduction in gases to the presence of complex tripartite systems of charged molecules (see Note) rather than to that of atomised ions. Exact work in this direction would be most valuable at the present time;

speculative discussion of uncertain results cannot determine the nature of the process of "ionisation," so called.

(NOTE.—It is not customary, I believe, to drag in dissociated ions to explain the action of a condenser; we are satisfied to think of the collection of a charge as dependent on the displacement and distortion—the polarisation—of the molecules in a viscous electrolyte of low conductivity).

CALCIUM: ITS PROPERTIES AND POSSIBILITIES.*

By ARTHUR E. PRATT, B.Sc., A.R.S.M.

General Properties.—Calcium is a silvery white metal readily oxidised in moist air. It is very light (sp. gr. 1·52), fairly malleable, has a high specific heat, and is a good conductor of electricity. It is about as hard as aluminium, but at 400° C. becomes as soft as lead. It is volatile, and can be sublimed *in vacuo* between 700° C. and 800° C., and melts at the latter temperature. It is a very powerful reducing agent.

Calcium Alloys.—The chief effects of alloying calcium with other metals are to produce brittleness, crystallisation, and hardness; to promote oxidation and disintegration on exposure to air; to confer the power of decomposing water and in other ways increasing the chemical activity.

The author's experiments confirm Roberts-Austen's observation that the presence of small amounts of metals of high atomic volume will cause deterioration of the physical properties of metals of low atomic volume. The atomic volume of calcium is high (25·4), and the effect of small amounts on other metals is decidedly prejudicial, provided that the metals in question are pure. The experiments were conducted in a converse manner to Roberts-Austen's, *i.e.*, the constant was a metal of high atomic volume (calcium) instead of being low (gold). In the course of the work the following observations were made. When an alloy is made of calcium and some metal which possesses a chemical property in common with it, an increased activity in the manifestation of that property is noticed in the alloy. This increase appears to be greater than would be obtained by the simple admixture of a more active metal, the presence of calcium usually increasing the activity of the other metal. In some cases the alloy is more active than either of its constituents.

Further, the chemical properties of calcium appear to be more pronounced in an alloy with a metal having an atomic volume closely approaching that of calcium than they are in an alloy of the same percentage with a metal having a much lower atomic value. The two metals in question should be about equally active when unalloyed in the particular property with respect to which they are to be compared.

It is probable that both these principles are general, and not confined to calcium, although more extended research on these lines would be desirable.

Industrial Possibilities.—The most promising applications of calcium are as a reducing agent and for the refining of metals. In the latter case it acts in three distinct ways:—(1) By reducing oxides and sulphides; (2) by eliminating dissolved gases; (3) by forming compounds with certain impurities, thus rendering them less deleterious. All three modes of action are strikingly shown in the case of copper. A suitable addition of calcium will remedy "dry" or "sulphury" copper, give a sound casting, and give a soft and tough ingot with prohibitive proportions of bismuth or antimony, besides restoring ordinary overpoled copper to tough pitch. If excess of calcium is present, however, it induces brittleness on its own account.

With one or two doubtful exceptions, no alloy of calcium has shown any promise of commercial utility so far as physical properties are concerned, its only likely application in this direction being its hardening property.

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

ON SUBSTANCES WHICH FORM THREE DIFFERENT LIQUID PHASES.*

By Dr. F. M. JAEGER.

THE results now recorded arose originally during an experimental investigation into certain theoretical objections which occurred to the author in connection with Bömer's method for detecting the adulteration of animal fats with vegetable fats. During this work the series of fatty esters of cholesterol and of Windaus's two phytosterols of Calabar fat were prepared, and the observation of the brilliant colour changes which occur on melting the cholesterol esters led to the study of the liquid phases of these substances. The colour changes in question occur with greatest brilliance with cholesteryl cinnamate, and were demonstrated to the audience.

The colour changes are due to the fact that the substances which exhibit them yield on melting several strongly doubly refracting liquid phases; the liquid phase stable at higher temperatures is always singly refracting. Lehmann showed by the micro-crystallographic examination of the caproic ester that two doubly refracting liquid phases exist, and that of these one is in meta stable equilibrium with the solid substance.

The author has, however, found that in the cases of a number of the esters in question three liquid phases occur, and are in perfectly stable equilibrium with the solid phase; of the three liquid phases two are doubly refracting, and consist of aggregations of liquid crystals, whilst the third is always singly refracting, but often much more viscid than the doubly refracting phases. The colour changes occur at the transition temperatures—or, rather, at a few degrees below those temperatures—whilst the two liquid layers are separating from each other.

The transitions of phase are in many respects analogous to those occurring with polymorphous substances, so that stable and metastable equilibria and therefore also cases of monotropy and enantiotropy occur. It is, however, remarkable that a new kind of equilibrium is observed with these substances; this the author terms "prostable equilibrium." A prostable phase resembles a metastable phase in that both can be experimentally realised only as the result of a temperature change in one direction; the two kinds of phase differ in that the prostable phase can only be obtained as a result of raising the temperature. The formation of a prostable phase therefore occurs before and after that of the stable phases during a rise of temperature. This was demonstrated to the audience with the aid of cholesteryl laurinate and illustrated by means of the vapour-tension curve of the ester.

With some of these esters the author has further observed that the solid phase can be heated to above the melting-point without melting; cholesteryl laurinate can thus be heated to 5° above the highest transition temperature without the solid phase entirely disappearing. Similar retardation phenomena occur in other cases, and their occurrence can be conveniently illustrated by means of the vapour-tension curves of the α-phytosterol esters.

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

Alloys of Nickel and Tin.—Em. Vigouroux.—When mixtures of nickel and tin, containing between 40 and 50 per cent of the latter, are heated in a current of pure hydrogen, from the resulting product a compound of the composition Ni_3Sn_2 may be isolated by the action of hydrochloric acid. The alloy is very easily crushed in a mortar and fragments of it may be broken off with the fingers.—*Comptes Rendus*, cxlv., No. 4.

ANALYSIS OF PRODUCER GAS FOR THE POWER ENGINEER.

By H. PROCTER SMITH, F.C.S.

In the writer's opinion there is nearly always a gap between the results given by a chemist and the data required by an engineer to act upon the information given, and, as a rule, this gap can be filled much more easily by the chemist than by the engineer, and if it *were* filled by the mutual co-operation of the chemist and the engineer there is no doubt that valuable information would be acquired, and would eventually bring the chemist and the engineer to be recognised as main factors in helping to swell the profits of an industrial concern, and not as at present mere "non-producers" and a necessary nuisance.

This is illustrated in a very striking manner since the rapid advances which have been made in utilising producer gas as a motive-power in a gas-engine.

In this instance we have a chemist who makes analyses of samples of the gas and perhaps offers suggestions as to the reason for an increased percentage of carbon dioxide, or of hydrogen, and so forth, and who reports to the engineer the relative quantities of carbon dioxide, carbon monoxide, hydrogen, marsh gas, &c., but, as a rule, this is all.

Now, the engineer knows that he wants a gas with as large an amount of combustible as possible, and also knows that the gases, carbon monoxide, hydrogen, and marsh gas are combustible, but from looking at the mere percentages of these gases he cannot, as a rule, form much idea of the amount of horse-power which this gas will develope in his engine, and the factors given below are such as will enable either the engineer or the chemist to rapidly convert the gas analysis into a heat analysis, and from that to a power analysis.

The power capable of being developed by a gas is a ratio of its heating value, and this value is in relation to the amounts of its constituent gases. An element when combining with oxygen evolves a certain definite amount of heat, and if this change is brought about rapidly also light, when the process is termed "combustion."

With the commoner elements—carbon and hydrogen—use is made of this reaction to generate heat, and the elements are termed *fuels*. Coal is a mineral consisting chiefly of carbon and hydrogen, and may be ignited and burnt in air with the generation of heat. Coal may also be partially burnt in a closed vessel termed a "gas producer," and converted into gas which may be burnt and converted into power apart from the vessel in which the gas is generated.

The amount of heat so generated is expressed in two chief units, viz. :—

British Thermal Unit (B.T.U.), which is the amount of heat required to raise 1 lb. of water 1° F.

Kilogramme Calorie, which is the amount of heat required to raise 1 kilogrm. of water 1° C.

The water in each case being at its point of maximum density, 39·2° F. or 4° C.

The heating or calorific value of carbon is 14,544 B.T.U.; that is to say, if 1 lb. of carbon was burnt in oxygen or air it would generate enough heat to raise 14,544 lbs. of water 1° F.

To consider now the combustible gases :—

	B.T.U. per lb.
Carbon monoxide	4,386
Hydrogen	61,524
Marsh gas..	24,021

That is, the heat generated from the above gases in *parts by weight*; but as we generally measure gas these figures require to be converted into the B.T.U. or calories which are developed by burning 1 cubic foot or 1 cubic metre of the gas.

Further, in burning all substances containing hydrogen the combustion produces water, and if, as is generally the case, the final temperature is above 212° F., that water is converted into vapour (steam) and passes off in the waste gases. Now, the conversion of water at 212° F. into steam at 212° F. absorbs a large amount of heat termed "latent heat," which can only be recovered by condensing the steam, and thus the *available* calorific value produced by burning hydrogen is lowered, and therefore in all compounds containing hydrogen we have a *total* and an *available* calorific value.

The following factors serve to convert any of the gases, hydrogen, carbon monoxide, or marsh gas, directly into terms either B.T.U.'s or calories :—

	B.T.U. per cubic foot.		Kilogrm.-calories per cubic metre.	
	Total.	Available.	Total.	Available.
Carbon monoxide	3·419	3·419	30·43	30·43
Hydrogen	3·473	2·924	30·91	26·026
Marsh gas.. ..	11·278	10·133	100·38	90·225

To convert
- Calories per cubic metre into B.T.U. per cubic foot multiply by 0·11235.
- B.T.U. to calories multiply by 0·252.
- Calories to B.T.U. multiply by 3·968.

To show how such a calculation may be worked, suppose we have a sample of Mond gas of the following composition :—

	Per cent.		B.T.U. per cubic foot.	
			Total.	Actual.
Carbon dioxide..	12·9 ×	—	Nil	Nil
Carbon monoxide	13·2 ×	3·419	45·14	45·14
Hydrogen	24·8 ×	3·473 or 2·924	86·13	72·51
Marsh gas.. ..	2·3 ×	11·278 or 10·133	25·94	23·30
Nitrogen	46·8 ×	—	Nil	Nil
	100·0		157·21	140·95

Thus, by a few very simple calculations it is possible to convert a chemical analysis into a heat analysis.

Then for power conversion :—

1 B.T.U. = 778 foot-lbs.

1 Horse-power = 33,000 foot-lbs.

Thus, the *theoretical* power analysis is merely a matter of proportion.

It must, however, be borne in mind that the theoretical and practical results, otherwise the efficiency of the best heat engine of this type, seldom exceeds 25 per cent, but to the gas-power engineer the calorific power rather than the chemical analysis of a gas is what is required.

The Fresenius Chemical Laboratory at Wiesbaden.—During the Summer Term, 1907, the Fresenius Chemica Laboratory was attended by twenty-eight students. Of these, eighteen were from Germany, two from England, two from France, two from Holland, one from Hungary, one from Norway, one from Russia, and one from East India. There were three assistants in the Instruction Laboratory and twenty-four in the "Versuchsstationen" (Private Laboratories). To the certified staff of teachers belong the Directors, Geh. Regierungsrat Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz; also Prof. Dr. Med. G. Frank, Dr. L. Grünhut, Dr. R. Fresenius, and J. Huber (Architect). The Winter Term begins October 15th. During the past term, besides the scientific researches, numerous analyses were undertaken in the different departments of the Laboratory (Versuchsstationen) in the interests of trade, industry, mining, agriculture, hygiene, justice, and government.

CONSERVATION OF HISTORIC BUILDINGS AND FRESCOES.*

By Professor A. H CHURCH, M.A., D.Sc., F.R.S.

THE title of this Discourse as announced is in one way too wide, in another too narrow. For "conservation of historic buildings" should be substituted "conservation of urban stonework," and for "frescoes," "wall-paintings."

We have to consider the nature of the attack and of the defence—the weapons and the armour—the damage and its repair.

First amongst the destructive agents at work, I am bound to place sulphuric acid. I own myself a *thiophobist*. Dr. S. Rideal has given an estimate of the amount of sulphuric acid poured year by year into the atmosphere of London by the coal burnt in the Metropolis. His minimum figure is half a million tons, his maximum twice that amount. But before dealing with this branch of the subject in some detail, let me enumerate the chief of the other hostile agents. These are soot and tarry matters from coal-smoke; water, and an abnormal amount of carbon dioxide. Minor enemies, such as hydrochloric acid, nitric acid, and ammonia salts, with sulphuretted hydrogen and sulphurous acid, may be put on one side for the nonce. These assist in doing damage—damage of a special kind and to particular materials, such as metals and organic pigments—but our attention ought to be focussed on the chief mischief-makers. Before dealing with these, I may observe that it is fortunate that nitric and hydrochloric acids exist in but small proportion in the atmosphere of towns, save in the immediate vicinity of certain factories. I say "fortunate," for at present no efficient chemical means of neutralising their bad effects upon stonework seems available. Of course, one may use mechanical methods of protection, but a stone which has been attacked by nitric or by hydrochloric acid does not allow of the entire conversion of its soluble salts into insoluble, nor, in consequence, of its reconsolidation.

Even now I cannot approach closely the story of our arch-enemy, sulphuric acid, without previously saying a few words about soot and tar, about water and carbon dioxide. The important *rôle* of these last in the natural weathering of stone does not need discussion, but water, as the carrier of sulphuric acid, and as the solvent of the sulphates which it helps to form, must not be passed by in silence. Moreover, the condensation of moisture upon the surface of a fresco within a building is most harmful, and, when it cannot be wholly avoided, indicates the desirability of applying some waterproofing material to the surface of the painting. As to soot and tarry matters just named, one has to remember that even the total abolition of smoke from coal would in no way lessen the amount of sulphuric acid produced in the burning of this fuel. The soot and tar of smoke do indeed adhere to stone and discolour and disfigure it, but, except as carriers of acid, they do not corrode it. Here are some figures from the analysis of a strange crust attached to the under-surface of the cornice above the colonnade and below the dome of St. Paul's Cathedral. This crust has been slowly formed by the conversion of calcium carbonate from the Portland stone above the cornice into gypsum. This change has been effected by the acid rain of the City; then the gypsum has entered into solution, which has hung as drip to the lower face of the cornice, until the water has evaporated, and the residual gypsum, dirty with 1 per cent of soot and somewhat less of tar, has formed a stalactitic mass, occasionally reaching 3 inches in depth. The phosphate of lime present has never been dissolved, but represents one of the constituents of the original stone mechanically carried down and entangled in this dark grey stalactitic gypsum. But a visit to St. Paul's is not needed to see what damage is wrought by sulphuric acid even upon Portland stone. Its decay, being regular and even, often passes unnoticed, but may be watched in all parts of London, in balconies, copings, quoins, &c.

Incrustation from Drip below Cornice, St. Paul's.

Carbon	1·01 per cent.
Ammonium sulphate ..	0·93 ,,
Tar..	0·60 ,,
Gypsum..	73·80 ,,
Calcium phosphate ..	2·22 ,,
Calcium carbonate ..	none

Allow me to direct your attention to the two chief sources of the sulphuric acid found in the atmosphere of towns, and especially in that of London. There is no doubt that the larger proportion of the sulphur present in coal escapes during burning in the forms of sulphuric and sulphurous acids. Some remains in the ash, and this quantity may be increased by mingling slaked lime with the coal. (Lime-water, which has been suggested for this purpose, is far too weak; indeed, 3000 gallons, or 13 tons 8 cwt., would be required to fix the sulphur of 1 ton of coal!) But there is a minor though by no means negligible source of sulphuric acid in the products of the combustion of coal-gas. Since the restrictions imposed on the gas companies of London have been relaxed—that is, since October 1, 1905—the sulphuric acid from this source has trebled in amount, the average during the twelve months preceding the relaxation having been 11½ grains per 100 cubic feet, but in the subsequent twelve months 33 grains. (I have to thank Dr. F. Clowes, Chief Chemist and Superintending Gas-Examiner to the London County Council, for his kindness in supplying me with the official figures). And during the present year so far there have been 43 grains in the same volume of gas. (The corrosion of copper-boilers heated by gas is now so much more rapid that their lives are shortened in the ratio 7 to 2). If sulphuric acid from coal-gas (like that from paraffin oil) contribute in a comparatively small degree to the pollution of the *general* atmosphere of London, yet it exerts a definitely injurious action when produced in close proximity to an easily affected surface, such as that of a fresco, *within* a building. No wonder that the delicate film of calcium carbonate, the distinctive binding material in a fresco, soon perishes under the onset of oil of vitriol. And here let me anticipate, what I might have relegated to a later part of my discourse, namely, a few words concerning the best-known frescoes in the Palace of Westminster. I do this because the question of sulphur in gas happens to have been brought into close connection with these paintings in consequence of a Parliamentary paper published last year (Cd. 3085). For it has been urged, by one who writes in the interest of the gas companies, that "the hydrochloric and nitric acid vapours resulting from the electric arc-lamps in nightly use in London are even more pernicious than the burning of gas as at present manufactured." But it must be remembered that analyses of London air and London rain prove that the proportion of these acids present is quite insignificant compared with that of sulphuric acid. The same writer states that five frescoes in the King's Robing Room in Westminster Palace have required nothing more than the removal of dirt. This remark is made in order to discount a statement of mine in the Parliamentary Paper just named. This statement runs thus: "The increased and increasing consumption of coal in London, and the greater licence allowed to the gas companies in the matter of freeing their gas from sulphur compounds, must result in a serious augmentation of sulphuric acid in the air of the Metropolis." But very much more than the removal of dirt was needed. The frescoes are no longer frescoes. While retaining the aspect of frescoes, they have been transformed gradually into paintings which have had their original binding material replaced mainly by ceresin and paraffin wax, unalterable compounds competent to resist even sulphuric acid. But not only has the painted surface required fresh protection, but the ground itself has had to

* A Discourse delivered at the Royal Institution, April 12, 1907.

be strengthened by similar treatment, the plaster having been in many places "sulphated" and thus rendered rotten. So the writer in the *Gas World* of August 25, 1906, has *not*, as he says, hunted out "this mare's nest," and has *not* furnished a "typical illustration of the reason why what is called 'science' does not carry conviction when dragged into the concerns of everyday life."

And now I turn to another criticism of the already-quoted passage from the latest Parliamentary Paper on Westminster Frescoes. It will be found in the *Journal of Gas-Lighting* for the 21st of August last. The writer, after stating that he is not then disposed to question the opinion that it is sulphuric acid which is the chief destructive agency at work on the Westminster paintings, argues that the greater licence allowed to the gas companies will result in an improvement of the London atmosphere. The line of argument is this—"The use of gas will be extended by the cheapening which the slight increase in the permitted amount of sulphur in the gas involves," and in consequence less coal will be burnt, and there will, therefore, be less sulphuric acid produced and thrown into the atmosphere. For it is admitted on all sides that the burning of coal is the prime source of the sulphuric acid in the general atmosphere. Of course, if gas were made at or near the collieries, and sent in pipes to the big cities, and displaced coal for heating as well as lighting purposes, we should go far to abolish town smoke, and should greatly lessen the sulphuric acid. Unfortunately for the actual cogency of this argument, we find that the three chief gas companies in the county of London have NOT reduced the price of their gas in the smallest degree since the relaxation of the rule about sulphur, while their gas has, during the twelve months ending September 30, 1906, discharged into the air three times as much sulphuric acid (and during the last three months, four times) as it did under the former restrictions. This is, indeed, a retrograde movement.

One word more on this subject. The wall-paintings in the King's Robing Room at Westminster are, or rather were, true frescoes. Yet the *Westminster Gazette* stated, in one of its issues of August last, that a representative of the paper was told at the National Gallery that these works "were not real frescoes, but oil (paintings) on soft plaster." No person of experience and authority in Trafalgar Square could have made so absurd a statement. The paintings referred to, five in number, were executed in true fresco by William Dyce, R.A., four of them between the years 1851 and 1854, while the fifth and largest was completed in 1864.

Before going further, I would direct attention to the amount of calcium carbonate which the minimum quantity of sulphuric acid yearly produced from coal-burning in London might transform into gypsum: 500,000 tons of this acid might destroy 510,200 tons of $CaCO_3$, evolve 204,080 tons of CO_2, and produce 877,544 tons of gypsum. This change is, moreover, accompanied by an expansion, 100 vols. of calcite producing 120 vols. of gypsum. Happily, part of this sulphuric acid passes away harmlessly, yet the havoc done is everywhere conspicuous, on stone, marble, and mortar.

Thus far I have spoken about our chief agent of destruction, sulphuric acid, describing its sources and connecting it with stonework, on the one hand, and with certain mural paintings on the other. Now I purpose dealing with certain preservative and restorative methods, taking, in the first place, stonework into consideration, then mural paintings. My aim will be to describe two methods of treatment only—methods which are not always available, though of wide application.

In reference to decayed stonework, I would name the opening section, "Baryta *versus* Lime." Some persons interested in the preservation of old buildings, and rightly refusing the ignominy of a coat of common oil-paint or of prosaic cement, recommend treating the decayed and decaying stone with lime-wash (not whitewash). The suggestion is an obvious one, but unfortunately this easy process is unsound in theory and ineffective in practice. Moreover, the application of this meagre and indiscriminate lime wash destroys all the exquisite qualities of tone, colour, texture, and translucency which old stonework may still possess in its age-worn state. And it cannot fail to distort and even obliterate the last surviving traces of surface-enrichment, of mouldings and carvings (*e.g.*, the decaying diaper-work in the spandrils of the great arches in Westminster Abbey). Lime forms a crust on the decayed stone; lime does nothing towards the consolidation of the disintegrated substance; lime is itself subject to the same chemical changes which have injured the stone; lime sooner or later falls off, bringing with it the decayed layer to which it was applied. Mr. Thackeray Turner, one of the most strenuous apostles of the gospel of lime-wash, cited (*The Times*, November, 1904) the case of lime-washed cottages in Wales and Cornwall as evidence of the preservative value of this treatment. But as we are dealing with urban, not rural conditions, such evidence is beside the mark. Baryta, it is true, is a late-comer compared with lime, but it has been used, though in a half-hearted way, for forty-five years. Had it been known earlier to the advocates of lime, it ought to have ousted that earth ere now. Having the choice of two earths, why not use the better? Please visit the eastern walk of Westminster Cloister, and look at what has just been done to the ribs and vault of the bay nearest to the Abbey; no London dirt can turn that prose into poetry.

Let me describe the theory and practice of the baryta treatment of decayed stone. Baryta-water only is used, the liquid being applied, when all dust has been blown away, in the form of extremely fine spray, on very tender surfaces. Where the stone will bear it a rose syringe or even a brush may be used. Indeed, after a few sprayings and the lapse of a week or two, it is generally feasible to adopt the rougher methods. The rationale of the action of baryta is simple. The liquid, which saturated at 16° C. contains about 3 per cent of BaO, is absorbed by the decayed stone, penetrating to some depth, maybe 2 or 3 inches. The baryta forms an insoluble sulphate with the sulphuric constituent of the gypsum and of the other sulphates present, and at the same time calcium hydrate is set free. This probably in part unites with soluble silica, but most of it gradually becomes carbonated, while the calcium carbonate thus regenerated actually reconstitutes the original binding cement of the stone. This description applies especially to sandstones compacted by calcium carbonate; but limestones illustrate the same changes. Unlike water-glass and most of the other preparations which have been used for hardening decayed stone, baryta forms no crust on the surface—indeed, it produces no sensible effect on the outside until it has penetrated to the deeper parts. So when the Dean of Exeter, in his letter published in *The Times* of October 26 last year, stated that "baryta does not strengthen the stone structurally, it forms a scab of the decayed stone on the face of the sound stone, which, as is the case with all scabs, has a tendency to peel off," he could hardly have selected more inappropriate terms in which to describe the action of baryta. The Dean further stated his belief "that the decay at Westminster was comparatively superficial." Surely very few persons would regard a decayed layer 2 or even 3 inches thick as superficial. And he raises the question whether the baryta-treatment, which his friend the late Mr. Micklethwaite told him seems to be successful "so far as we can judge yet," would answer outside a building as well as inside. Here I may cite the case of Chichester bell-tower. On analysing portions of decayed stone from the several faces of this campanile, I found sufficient sulphate present to warrant the application of baryta water to a trial area. This was done some two or three years ago with so satisfactory a result that last July Mr. Somers Clarke, the architect, decided upon treating the whole of the octagon and the entire north face of the tower in the same way. He wrote:—"The success of the experiment fully justifies this course." There is no need to multiply references to other successful trials of the

use of baryta in strengthening external decayed stone-work and stopping further damage, but in the course of the next few years it may be expected that many favourable reports will be forthcoming. Experiments, large and small, are being and have lately been made, and promise well. I have been told of a single failure, but I learnt that the architect in charge expected that the consolidation of the decayed stone would be immediate, and had not waited for the few weeks needed for carbonation to take place. It is proper to add that where decay has resulted from simple weathering—the action mainly of water and carbon dioxide—or from sea-salt, the treatment with baryta is not applicable. Nor should it be forgotten that baryta water is toxic and easily spoilt by exposure to the air. Then, again, there may be too little gypsum present in the decayed stone for an adequate liberation of caustic lime to occur. Without laying down a rule it may be said that where so much as 2 per cent of this sulphate is present, baryta treatment is indicated.

In the case of the Chapter House, Westminster, to which I would now direct your attention, the proportion of calcium sulphate was far more than enough to fulfil this condition of success. Although the exterior of this building, and most of the upper portions of the interior, date only from the time of the restoration carried out by Sir Gilbert Scott, much of the original work of the middle of the thirteenth century remains. The Chapter House is in the custody of H.M. Office of Works. The successive First Commissioners, as well as the permanent officers of that Board, have sympathetically regarded its preservation So when, in 1900, Mr. Micklethwaite pointed out to Mr. Akers Douglas that serious tokens of disintegration were appearing in the early mouldings of the arcading, in the diaper work above, and in the exquisite sculpture of the soffits of the entrance arch, my advice was asked. A few experiments showed that the disintegration and efflorescence were due to the formation of gypsum, which, in some parts of the decayed material, exceeded 17 per cent. The stone, a sandstone, with a calcareous cement, and known as firestone and Reigate stone, no longer contained any calcium carbonate—indeed, had an acid reaction, and yielded to water 4 per cent of saline matter other than gypsum.

Reigate Firestone.

	From the quarry.	From the Chapter House.
Calcium carbonate	9·2 per cent	None
Gypsum	Trace	17·85 per cent
Chlorine	Trace	0·37 ,,
Ammonia	Trace	0·05 ,,
Reaction ..	Neutral	Acid

You will recollect that the conversion of calcium carbonate into gypsum is not only accompanied by the evolution of much carbon dioxide, but that 100 volumes of the former compound expand into 120 volumes of the latter. The rationale of the baryta treatment, to which the interior stonework of the Chapter House was submitted, has been already described; but it may be added that the operations were commenced in May, 1900, continued in 1901, and completed in 1903. Before treatment, a touch of the finger sufficed to bring away the surface of the carving, afterwards the stone was as sound as that newly quarried, and harder. Incidentally it was found that decayed Purbeck marble was equally amenable to treatment; a column at the right-hand wall of the entry having been successively *barytised*. In no instance has there been a sign of subsequent deterioration. Full particulars are to be found (of the operations in the Chapter House) in the Parlimentary Paper, Cd. 1899/1904. It may be of interest to mention that 220 gallons of baryta water sufficed to treat 560 superficial yards in the Chapter House and its inner entry, eight applications being generally made. The cost of the material was quite trivial, the expense of the treatment being practically confined to the cost of labour and scaffolding. Let me add that the cheapest and best source of the baryta is the fused crystalline hydrate, which contains about 58 per cent of oxide, is less liable to carbonation than the ordinary crystals, and corresponds to the formula $BaH_2O_2,5H_2O$.

With regard to the treatment of the decayed limestone of Canterbury Cathedral, and especially of Bell Harry Tower, a few words only are required. Between November, 1901, and June, 1902, I made a series of analyses of decayed stones from this tower, and recommended the architect in charge to adopt the treatment with baryta, as an experiment on a small surface. This was to have been done in the summer of 1902, but I heard nothing further of the matter until more than two years afterwards, when I learned that, under other advice, the discredited process of the late Jesse Rust, described in his incompleted Patent of June 6, 1861, alternate washes of baryta and fluosilicic acid, but modified by using the fluosilicic acid in smaller proportion than he recommended, was to be tried alongside of the simple baryta solution. I have always deprecated the application of a free acid, such as fluosilicic, to stone-work injured by sulphuric acid. For it liberates carbon dioxide from any carbonates present, and at least sometimes produces an unsightly white efflorescence. My own patent process of 1862, according to which alternate applications of baryta-water and of a dialysed solution of silica were to be made, causes no efflorescence and no liberation of CO_2, and has been used with success on large surfaces of new stone. But the silica clogs the pores of the stone, and, if employed at all, should be reserved for the final dressing. My own convictions as to the best course to be pursued at Canterbury, as expressed in my letter to *The Times* of November 19, 1904, remain unaltered in the main, although there are cases in which a hydrofuge substance, such as paraffin or ceresin, may be safely used. But I have never found baryta to fail, where its employment was indicated, on calcareous stone. Nor does disruption ever occur with the repeated but reasonable application of baryta-water saturated at 16° C., although I can easily believe that warm and stronger solutions might be dangerous to use.

Last year five bays of the Cheapside frontage of Mercers' Hall were treated with baryta. The stone was suffering from serious decay, so that some loose portions had to be removed. The treatment with baryta was followed, in the case of the three easternmost sections of the frontage, by another treatment intended to render the re-consolidated stone acid-proof. I had used the second method with apparent success, in protecting mural paintings in Westminster Palace. It consists in applying to the surface a paste or ointment of ceresin, a solid paraffin wax from ozokerite. The sample used had a solidifying point of 156° F.; it was made into a paste by taking 4 parts by weight, and melting them in the presence of 1 part of terpene and 16 parts of toluol. The mixture is spread on the stone, and then, after the lapse of twenty-four hours at least, the residual layer of ceresin is driven by heat into the stone. There results a slight deepening of the colour of the surface and a slight marble-like translucency. These changes of tone and colour may be seen on Mercers' Hall by comparing the untreated, the baryta-treated, and the double-treated parts. Ceresin produces a better result than the more crystalline paraffin of the same solidfying point, though the latter is perhaps less liable to be soiled by smoke. It is essential to the success of the double treatment that the calcium hydrate set free by the baryta should be allowed time to become carbonated before the ceresin-paste is applied. The advantage of associating the two treatments lies in this, that while the baryta repairs the damage done by sulphuric acid and reconstitutes the stone structurally, the ceresin waterproofs the surface and prevents further corrosion. Needless to say, it is wiser to waterproof a sound rather than a crumbling stone. What Sir Gilbert Scott tried to do in Westminster Cloisters, with his very perishable so-called preservative, shellac in spirit, was the latter, and led to unhappy results. Thus, even ceresin or paraffin cannot be always recom-

mended, notably where soluble salts and moisture are present. To coat the outer weak layer of stonework decayed to some depth tends to form an easily detachable crust.

However, ceresin alone has been used with apparent success so far in the case of the local Camaru stone of which the Bank of Australasia at Melbourne is built. After due laboratory experiments I recommended this treatment in February, 1903. Mr. Anketell Henderson, the Melbourne architect, tried aluminium oxalate and other solutions, but found, he says, "that ceresin alone resisted the wet of our torrential rains and the erosion of our sandstorms." He emphasises the use of a ceresin of high melting-point to obviate tackiness, and employs an electric heater in his spraying apparatus. Ordinary oil-paint, frequently renewed, fails to preserve the stone in question. Even a solution of ceresin in petrol proved too weak.

We will now turn to the conservation of mural paintings. Besides ordinary oil-painting four methods are, or were, in common use—tempera or distemper, true fresco, stereochrome or water-glass, and the so-called spirit fresco of the late Mr. Gambier Parry. The last-named process or method need not detain us, for, so far, the paintings executed in this way, if the ground or plaster have been properly prepared and protected, require nothing further than cleaning with bread. And if they should suffer injury or need further protection, the diluted medium can be used for these purposes. Owing to causes explained in memoranda addressed to H.M. Office of Works, the two well-known lunettes by Lord Leighton (Arts of Peace, 1881-6, and Arts of War, 1870 80) in the Victoria and Albert Museum, have required cleaning and repairing in the manner indicated. But the long series in the Ambulatory of the Royal Exchange, having been painted on canvas and affixed afterwards to a sound slate backing, have needed no restoration.

The English mediæval wall-pictures found chiefly in churches, but not unknown in secular buildings, are commonly but wrongly called frescoes. They were painted on dry plastered walls with pigments mixed with size or egg-vehicles. By the mistaken use of varnish, by over-drying when on panel, by mechanical injuries, by vibration, by the chemical action of a corrosive atmosphere, and by the penetration of damp or salts from behind or from below, such paintings have generally suffered serious changes, and are sometimes beyond repair. However, there are several ways of consolidating the painted surface and of securing it in position. Before describihg these, and how to choose, in any given case, the most suitable, I would urge the importance of precautionary measures, namely, the disuse of gas, the shutting off from the back and foundation of the wall of all sources of damp, and the avoidance of all further accession of soluble salts, such as nitre, ammonia compounds, Epsom salts, and common salt.

The very worst preparation that can be applied to a damaged distemper-painting on a damp or saline ground, is a spirit varnish such as mastic or shellac, or an oil varnish such as copal. Where damp and saline matters are present, a dilute solution (under 5 per cent) of pure gelatin in very weak spirit may be used; spraying with this liquid kept hot is often successful where the pigments are powdery. Another useful liquid is a 7 per cent solution of casein in very dilute ammonia, containing 1 per cent of glycerin. This preparation is particularly applicable for the treatment of distemper paintings on wood. But when the works to be treated are on a perfectly dry backing free from injurious saline matters, then, and then only, is it safe to apply what may be called a hydrofuge, or waterproofing material to the surface. This we have in the ceresin-paste already described. Occasionally an extremely small addition of copal varnish to this vehicle may be allowed to secure transparency. Indeed, in my earlier operations of this character I have used Gambier Parry's spirit fresco medium, leaving out the elemi, and replacing the beeswax by paraffin or ceresin. But wherever possible nothing but ceresin-paste or ceresin in solution should be employed. After the cleansing of the surface by an air-blast, by spirits of wine, and by bread-crumb, necessary repaints should be executed with powder-pigments mixed with egg-yolk; then the ceresin should be applied. Pigments to be avoided are yellow ochre, raw sienna, terre verte, and ivory black; zinc white should replace flake white.

With regard to the care of water-glass or stereochrome paintings, my experience, confined chiefly to those in Westminster Palace, has been described in full detail in three Parliamentary Papers, Cd. 7651 1895; Cd. 8054 1896; and Cd. 8893/1898. In these memoranda, the treatment of Maclise's great paintings in the Royal Gallery, and Herbert's picture of Moses and the Tables of the Law in the Peers' Robing Room, is explained. But the quite recent operations on other mural paintings executed in the same method may claim our attention for a few minutes. The sixteen pictures in the Peers' and Commons' Corridors, unlike the other wall-paintings in the building, have been protected for many years past by tightly-fitting glasses; still they have undergone, in part since they were glazed, some changes. The lime-plaster ground had become, in places, quite soft by sulphation, while the pigments were here and there powdery. Moreover, the grey bloom, which so often appears on stereochrome paintings, had overspread many large areas of these interesting and attractive historical works. This grey bloom had produced, in the seven pictures of the series which were dealt with last summer, a peculiarly unpleasant disturbance of the balance of light and shade. In many places, notably in the robes of the figures, the deep-shaded portions of the folds had become lighter in tone than the general surfaces intended to be fully illuminated. I have said that in the seven pictures dealt with in 1906 some of the colours were powdery, the pigments chiefly affected being yellow ochre, raw sienna, artificial ultramarine, and ivory black. This class of decay was seen at its worst in the picture in the Commons' Corridor by E. M. Ward, "The Landing of Charles II. at Dover, 1660." A list of the seven paintings cleaned and repaired in 1906 may prove useful for reference. And I would beg those of my audience interested in the subject to inspect the series, and to compare the untreated with the treated examples, premising that the condition of those dealt with was far more unsatisfactory than that of the rest:—

In the Peers' Corridor, four works by C. W. Cope, painted 1859 to 1866: "The Parting of Lord and Lady Russell"; "The Burial of Charles I."; "Charles I. erecting his Standard at Nottingham"; "Speaker Lenthall asserting the privilege of the Commons."

In the Commons' Corridor, three works by E. M. Ward: "The Last Sleep of Argyll"; "Charles II. and Jane Lane"; "The Landing of Charles II. at Dover, 1660."

The same methods of cleaning and reparation were adopted as in other cases. The grey bloom of silica and sulphate of lime was removed by oblique flicking with soft pads stuffed with carded cotton; cleaning with bread, distilled water, and spirits of wine removed dirt and saline matter. The weak places in the ground were consolidated by means of ceresin, while the whole surface finally received a slight protective film of spirit-fresco medium.

In the early part of this discourse I described, out of their proper place, the repairs executed in the five true frescoes by W. Dyce in the King's Robing Room. I now direct attention to another fresco. It was executed in 1872-3 in the church of St. Stephen, Sydenham Hill, by Sir Edward J. Poynter, P.R.A. It occupies a recess on the south side of the chancel. The artist had repaired it in tempera not long after its completion, but it subsequently showed signs of more serious deterioration. I found that the usual causes of injury had been at work. Much gas is burnt in the church, some burners being very near the picture. Soot, tar, cobwebs, and dust were first removed from the painted surface; then the weak places in the ground were strengthened by ceresin, and repairs

done in tempera colours. Finally, ceresin was applied to protect the restored picture.

There are many other cognate topics on which I should have wished to dwell, and other experiments which I should have been glad to show; but time fails me, and these experiments cannot be completed off-hand. But I may be allowed to state that my warrant for standing here to offer observations on certain methods for preserving stonework and paintings is derived from long devotion to these subjects. Half a century ago I read a paper on the induration of stone before the Oxford Architectural Society, while in January, 1862, I treated the same topic in a discourse delivered before the Architectural Association. About the same time I was trying experiments on the north front of Westminster Palace. A little later on, about 1865, I dealt with distemper paintings in Cirencester parish church and elsewhere. Waterproofing stone with paraffin wax, driven in by heat, was the subject of several trials in the later sixties. Afterwards the great fresco by G. F. Watts, in Lincoln's Inn Hall, was cleaned and repaired. This was in 1890. To the list may be added the works of Ford Madox Brown, in Manchester Town Hall, and other pictures and other buildings in various parts of the country, besides the long series of mural paintings in Westminster Palace.

I shall be glad if I have said anything to-night which will prove helpful in the preservation of mural paintings and the stonework in towns, especially in the case of historic buildings. The materials recommended are accessible, cheap, and easily applied. Doubtless there are other preparations available for the same purpose. Some of these may meet those conditions to which the materials I have recommended are not applicable.

NOTICES OF BOOKS.

Paper Technology. By R. W. SINDALL, F.C.S. London: Charles Griffin and Co., Ltd. 1906.

STUDENTS attending technical classes on the manufacture of paper will find this book a great help to them when revising their lecture work. While highly technical matter is omitted, a very readable account is given of the making of paper, and methods of determining its physical and chemical properties, which both paper-makers and users will find full of interesting matter. The determination of the chemical constituents of paper is discussed fully enough to enable the reader to get an elementary idea of the basis of the methods generally adopted, and the use of the microscope in the examination of paper is also explained. A useful glossary of trade terms will be appreciated by students, and the plates showing the fibres of different materials are a valuable addition to the book.

Solubilities of Inorganic and Organic Substances. By ATHERTON SEIDELL, Ph.D. New York: D. van Nostrand Company. London: Crosby Lockwood and Son. 1907.

THIS handbook of the quantitative determinations of the solubilities of all classes of substances is a valuable compilation. In all cases the author has referred to the original sources for his figures, in order to eliminate errors of quotation which might have crept into text-books, and in most cases he gives full references to his authorities, so that it would be an easy matter to look them up for experimental details if required. Moreover, in cases in which there are considerable discrepancies between the results of different investigators, an attempt has been made either by graphical methods, or else from theoretical or experimental considerations, to decide which results are probably more accurate, and these alone are tabulated in the book, which gives an admirably full and conveniently arranged list of solubilities in water and other solvents.

Radioaktive Umwandlungen. ("Radio-active Transformations"). By E. RUTHERFORD. Translated by M. LEVIN. Braunschweig: Friedrich Vieweg und Sohn. 1907.

THIS book is a translation of the Silliman Foundation lectures delivered by Prof. Rutherford at Yale University in March, 1905. The subject chosen for the lectures was the transformations of radio-active matter, and some account was also given of the general phenomena of radio-activity. Since the lectures were delivered many important discoveries have been made relating to radio-active changes, and the author has as far as possible brought the work up-to-date by additions and alterations. The translation has been done excellently, and Dr. Levin himself has in some cases added explanatory notes.

Die Chemische Analyse. ("Chemical Analysis"). Edited by Dr. B. M. MARGOSCHES. Vols. I. and II. Stuttgart: Ferdinand Enke. 1907.

THIS treatise on analytical chemistry, in which completeness is, above all things, aimed at, is to be issued in the form of monographs of convenient size. The author of each monograph will endeavour especially to give a comprehensive view of the branch of the subject entrusted to him, and the theory of analytical chemistry will be discussed, as well as the practice, in certain volumes of the series. The first volume contains a systematic account of the use of hydrazine in analysis, and has been written by Dr. Julius Schmidt. The uses of hydrazine and its salts in quantitative and qualitative work are first discussed, and then phenylhydrazine and its substitution products, and some other important derivatives of the parent substance are treated similarly. Special stress is laid upon the use of hydrazine in inorganic analysis, a use which is constantly being extended. The second volume by Dipl.-Ing. H. Nissenson is devoted to the determination of zinc, chiefly in ores of technical importance. Great prominence is given to the four methods, which were reported to give equally satisfactory results by the commission appointed to investigate the question, at the Sixth International Congress of Applied Chemistry at Rome, namely, Schaffner's process, Galetti's with potassium ferrocyanade, the gravimetric sulphuretted hydrogen method, and electrolysis, while other methods are also considered. Separation processes are included, and the monograph thus gives a full account of practically all reliable and convenient methods of estimating zinc.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

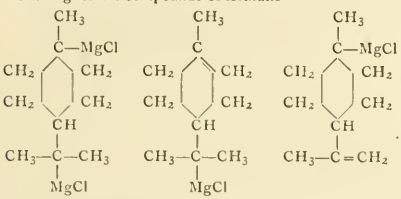
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 4, July 22, 1907.

Mixed Anhydride of Sulphuric and Nitric Acids.—Amé Pictet and Georges Karl.—Nitric anhydride dissolves in freshly distilled sulphuric anhydride with evolution of heat. When the product is distilled a thick liquid passes over between 218° and 220°. This liquid solidifies to a white crystalline mass on cooling; its melting-point is 124—125°. The same substance is obtained when solutions of the anhydrides are made separately in carbon tetrachloride and the two solutions are then mixed. The compound is very hygroscopic and fumes in air. It dissolves in water, evolving much heat, and giving a mixture of sulphuric and nitric acids. Analysis shows that the formula is $(SO_3)_4N_2O_5$, and hence it is probably a nitrosyl-tetrasulphate, $O<\begin{matrix}SO_2—O—SO_2—O—NO_2\\SO_2—O—SO_2—O—NO_2\end{matrix}$. The analysis

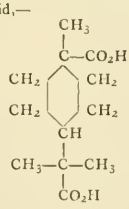
was performed by dissolving a known weight of the substance in water, determining the sulphur as barium sulphate, the nitrogen by Kjeldahl's method, and the total acidity by titration. When this substance is allowed to act upon organic compounds, complex products are formed, the nitration being accompanied by sulphonation, by oxidation, and by carbonisation. The authors have not succeeded in finding any liquid in which the mixed anhydride dissolves without attacking it.

Compounds of Nickel and Cobalt with Boron.—Binet du Jassonneix.—If mixtures of nickel or cobalt and boron are heated to 1100° or 1200° in a current of hydrogen, products are obtained which in their properties and structure recall the corresponding compounds of iron. The cobalt product, which contains about 5 per cent of boron, is attacked very slowly by warm hydrochloric acid. The residue then left contains 8·5 per cent of boron, and consists of the compound Co_2B. The corresponding nickel product does not yield a definite boride when treated with hydrochloric acid. If an ingot of the melt is used as anode in a solution of nickel chloride and a current is passed, the anode rapidly yields a metallic powder with composition corresponding to the formula Ni_2B. When the amount of boron exceeds 20 per cent, products are obtained which are more fusible than those which contain iron. The highest percentage of boron reached in these compounds is 27·1 and 27·2 respectively, corresponding to CoB_2 and NiB_2.

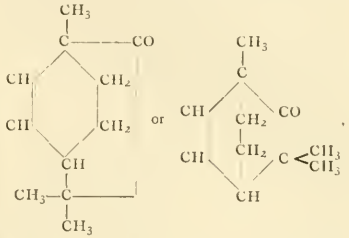
Menthane 1 . 8-Dicarboxylic Acid. A New Bicyclic Ketone.—Ph. Barbier and V. Grignard.—The action of powdered magnesium upon an ethereal solution of dipentene dichlorhydrate gives one dimagnesium and two monomagnesium compounds of formulæ—



and at the same time a hydrocarbon is formed, which appears to be dipentene. When carbon dioxide acts upon the mixture of magnesium compounds and water is added, one dibasic and two monobasic isomeric acids are formed. The first is easily separated by shaking the ethereal solution of the free acids and the hydrocarbon with sodium bicarbonate, while the monobasic acids can be extracted by the action of dilute soda. The dibasic acid is menthane 1 . 8-dicarboxylic acid,—



which can exist in two forms, both of which the authors have isolated. The *cis*-acid loses water when boiled with acetic anhydride, giving the anhydride $C_{10}H_{18}{<}\overset{CO}{CO}{>}O$, which yields a viscous product when it is subjected to distillation under atmospheric pressure. From this viscous product a ketonic liquid with the formula $C_{11}H_{16}O$ separates on rectification *in vacuo*. Thus, the decomposition of the anhydride proceeds as follows:— $C_{10}H_{18}{<}\overset{CO}{CO}{>}O = CO_2 + H_2 + C_{11}H_{16}O$. The new ketone may be represented by the formula—



and it is thus 1 . 3 . 3-trimethyl-1 . 7 . 8 . 4-bicyclo-5 . 2-hexanone.

New Silicide of Platinum.—P. Lebeau and A. Novitzky.—At a bright red heat a mixture of finely-divided silicon and platinum yields a compound, much heat being evolved, so that the incandescence of the mass visibly increases. Finally, an ingot looking like silicon is obtained, the polished surface of which reveals distinctly the existence of two homogeneous substances. One of these is silicon, and by the action of dilute potash the other constituent can readily be extracted. Its analysis gives the formula $SiPt$. This compound can be obtained in the crystalline state, and in its chemical properties it closely resembles platinum. It fuses, however, much more readily than platinum, its melting-point being about 1100°. It dissolves completely in aqua regia, and is more readily attacked by oxidising agents than platinum is.

General Method of Preparing Anhydrous Metallic Borides from Oxides.—F. Bourion.—At a temperature below a red heat hydrobromic acid converts oxides which are easy to reduce, such as those of nickel and cobalt, into anhydrous bromides, and also the oxides of the rare earths. The preparation is rendered easier if small quantities of sulphur chloride are added to the acid. This chloride is totally converted into bromide, and acts as a diluent to the acid and effects the conversion of the whole of the oxide into bromide; when hydrobromic acid alone is passed rapidly over the hot oxide the transformation is incomplete owing to the pastiness of the mass. Moreover, the sulphur bromide reacts on the water-vapour formed and regenerates hydrobromic acid, and the rate of the reaction is increased. The sulphur chloride must be heated to between 60° and 90°. The bromides thus prepared from oxides include the following compounds:—$ThBr_4$, $CrBr_3$, $NiBr_2$, $CoBr_2$, $NdBr_3$, $CeBr_3$, $ThOBr_2$, $LaBr_3$, $SmBr_3$, $PrBr_3$, $GdBr_3$, $DyBr_3$, $YtBr_3$, $TbBr_3$; the last eight compounds being obtained for the first time.

MISCELLANEOUS.

German Colonial Society Prize.—The President of the German Colonial Society offers a prize of £150 for a method to produce an extract from mangrove bark that will impart as light a colour as possible to leather and will only slightly darken by exposure to light. The mangrove bark contains a large amount of tannin and also a red colouring matter that prevents the bark and its extract from successfully competing with other tanning agents. The problem to be solved is the practical removal of this red colour. Competitors are invited to send in their methods by July 20, 1908, to Deutsche Kolonialgesellschaft, Schellingstrasse 4, Berlin.—*Chemist and Druggist.*

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Lecturer—OLIVER C. M. DAVIS, B.Sc, F.I.C.
Lecture Assistant—J. H. STURGESS.

The SESSION 1907-8 begins on OCTOBER 1st. Lectures on Inorganic, Organic, and Physical Chemistry will be delivered during the Session. The Laboratories are fitted with the most recent improvements for study and research in Chemistry and Metallurgy in all its branches. Several Scholarships are tenable at the College.

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LECTURES.

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Physical Chemistry .. .. { Prof. W. FRESENIUS, Ph.D.
Organic Chemistry.. .. .. { L. GRÜNHUT, Ph.D.
Chemical Technology .. .. { L. GRÜNHUT, Ph.D.
Microscopy, with exercises in Microscopic work .. .. { R. FRESENIUS, Ph.D.
Stöchiometry .. .. { R. FRESENIUS, Ph.D.
Chemistry and Analysis of Foods .. { R. FRESENIUS, Ph.D.
Hygiene .. .. { Prof. Dr. med. G. FRANK.
Practical exercises in Bacteriology.. { Prof. Dr. med. G. FRANK.
Technical Drawing, with exercises .. J. HUBER.

The next Session commences on the 15th of October. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to one of the Directors.

THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE, GLASGOW.

DEPARTMENTS OF CHEMISTRY, TECHNICAL CHEMISTRY, and METALLURGY.

Chemistry .. .. { Prof. G. G. HENDERSON, M.A., D.Sc., F.I.C.
Technical Chemistry .. .. .. Prof. THOMAS GRAY, D.Sc., Ph.D.
Metallurgy.. .. .. { Prof. A. HUMBOLDT SEXTON, F.C.S., F.I.C.

The Courses of Instruction in these Departments are arranged for Students preparing to become Manufacturing or Analytical Chemists, Metallurgists, or Science Teachers. The Courses in Chemistry qualify for the Examinations of the Institute of Chemistry, and of the Universities of Glasgow, Edinburgh, and London

SESSION 1907-8 begins on MONDAY, SEPTEMBER 23, in the New Buildings recently erected for the College. The ENTRANCE EXAMINATION begins on MONDAY, SEPTEMBER 16.

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16, NEWCASTLE ST., FARRINGDON ST., E.C.

THE CHEMICAL NEWS.
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(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following five subjects:—(1) English—Composition, Précis Writing, salient facts in English History and Geography. (2) Elementary Mathematics. (3) Latin or Elementary Mechanics, or Elementary Physics—Heat, Light, and Sound, or Elementary Chemistry, or Elementary Botany. (4) and (5) Two of the following subjects, neither of which has already been taken under Section (3). If Latin be not taken, one of the other subjects selected must be another Language from the List, either ancient or modern:—Latin, Greek, French, German, *Arabic, *Sanskrit, *Spanish, *Portuguese, *Italian, *Hebrew, and *Zoology, Ancient History, Modern History, Logic, Physical and General Geography, Geometrical and Mechanical Drawing, Mathematics (more advanced), Elementary Mechanics, Elementary Chemistry, Elementary Physics—Heat, Light, and Sound, Elementary Physics—Electricity and Magnetism, and Botany. Candidates in subjects marked with asterisk must give at least two months' notice before the commencement of the Examination.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Several valuable Scholarships and Exhibitions are available to students.

Intermediate Examination in Science.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry candidates are required to show a general acquaintance with General Theoretical Chemistry, Chemistry of Carbon Compounds, Physical Chemistry, and History of Chemistry since the time of Boyle.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

Doctor of Science.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Preliminary Scientific (M.B.) Examination.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S.
Lees Reader in Chemistry—G. Brereton Baker, M.A.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. Watts, M.A., and J. E. Marsh, M.A.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.
Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrary, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

Trinity College.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C S.

Junior Demonstrator—W. R G. Atkins, B.A.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students The Laboratories will open on October 1st. Lectures will commence about November 1st.

The Laboratories and the Lectures ofthe Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are :—

1. *Inorganic Chemistry and Chemical Philosophy.* — Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry.* — General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry.*—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins early in April and terminates about the end of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. These Foundation Scholars receive £20 per annum, have free commons, their chambers for half the charge paid by other students, and their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(Division of Engineering and Applied Science).

Senior Professor of Chemistry—J. M. Thomson, LL.D. F.R.S.

Professor—Herbert Jackson, F.C.S.

Lecturer and Demonstrators—P. H. Kirkaldy, F.C.S., D. Northall Laurie, F.C.S , S. W. Collins, and L. Hinkel.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1907-1908 are Oct. 2, Jan. 8, and April 29.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Fees.—Chemistry: Winter Session, £5 5s.; Summer Session, £3 3s. Practical Chemistry: Winter Session, £8 8s.; Summer Session, £4 4s. Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; One Term, £10 10s.; Two Terms, £18 18s.; Three Terms, £26 5s. Three days a week: One month, £2 12s. 6d.; One Term, £6 6s.; Two Terms, £11 11s.; Three Terms, £15 15s.

For fuller details the separate Syllabuses provided for each class should be consulted.

Metallurgy.

Professor—A. K. Huntington, A.R.S.M , F.I.C., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course.

Photography.

Lecturer—Prof. J. M. Thomson, LL.D., F.R.S.

For particulars apply to Prof. Thomson.

Evening Classes.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

Faculty of Science.

Professors—Sir William Ramsay, K.C.B., LL.D., F.R.S. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—E. C. C. Baly, F.I.C.; N. T. M. Wilsmore, M.Sc.; Kathleen Burke, B.Sc.; R. W. Gray, Ph.D.; and S. Smiles, D.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 1 to December 20; Second Term, from January 14 to March 27; Third Term, from April 28 to July 8.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Thursday, 2 to 3 30, or 3.30 to 5. Fee, £1 0 10s.

This Course treats of the chief physical and chemical

characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

In this Course the physical principles bearing on Chemistry are first discussed, and the Chemistry of the Elements and their compounds is treated in considerable detail, under the headings—Elements; hydrides, halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Course of Physical Chemistry.

October to February: Tuesday and Thursday at 9. February to June: Monday and Saturday at 9.

The Principles of Chemistry will be specially considered, comprising the Atomic Theory, Chemical Classification, the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent Chemical Theory researches.

Fees:—Courses £5 5s.; Term, £2 2s.; for a second course, £1 1s.

Senior Course of Inorganic Chemistry.

This Course will begin about the middle of February; Tuesday and Thursday at 9. Fee, £3 3s.

Electro-chemistry.

First Term, Monday and Saturday at 9. Fee, £1 1s.

Organic Chemistry.

Mon. at 12, Wed. and Fri. at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the Course of Physical Chemistry, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor of Chemistry—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—M. O. Forster, Ph.D., D.Sc.

Demonstrators—H. Chapman Jones; G. T. Morgan, D.Sc., A.R.C.S.; and J. C. Philip, M.A., Ph.D., B.Sc.

Assistants—G. S. Newth and Miss Whiteley, D.Sc., A.R.C.S.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Board of Education. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction lasts for three years, is the same for all the divisions during the first year, after which it is specialised according to the particular division in which the student is working for the Associateship.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject except Mining and Metallurgy and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	

The fee for the course of Mine Surveying is £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

The Session is divided into two Terms. The first Term begins about the first week of October, and ends about the middle of February. The second Term begins in the middle of February, and ends about the middle of June.

The hours of study are from 10 a.m. to 1.15, and from

2 to 4 or 5 p.m. every day, except on Wednesday and Saturday, when the College closes at 1 p.m.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixty-fifth Session will commence on Oct. 1, 1907.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C., F.R.S., (Dean); Botany (vacant); Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Director of the Edward Davies Chemical Laboratories and Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Assistant Lecturers and Demonstrators—A. Brooke, Ph.D. (Strass.), and T. C. James, M.A. (Cantab.), B.Sc.

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 1st, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1907-1908, Course A). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 18, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturer and Demonstrator, Alice E. Smith, B.Sc. Assistant Lecturer in Agricultural Chemistry, Alan Baguley, B Sc., F.I.C. Junior Demonstrator, J. O. Hughes, B Sc.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 3rd, 1907. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Inorganic and Physical Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Demonstrator—R. D. Abell, D.Sc.

Lecturer in Metallurgy—A. A. Read, F.I.C., F.C.S.

The Session commences October 8th, and terminates on June 26th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Organic Chemistry; Fee, £3 3s.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturer (Physical Chemistry)—James W. McBain, M.A.

Lecturer—Oliver C. M. Davis, B.Sc., F.I.C.

Lecture Assistant—J. H. Sturgess.

The session 1907-1908 will begin on October 1. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. A Laboratory has recently been fitted with a complete equipment for all ordinary measurements in Physical Cnemistry. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Registrar.

Day Lectures.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Introductory Course.—Three Lectures a week will be given during the First and Second Terms, and at least one Lecture a week during the Third Term. Fee, £3 13s. 6d.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Systematic Physical Chemistry.—Two Lectures a week will be delivered throughout the Session. Fee, £3 13s. 6d.

Electro-chemistry.—One Lecture a week will be given during the Third Term. Fee, £1 1s.

Advanced Course.—Two Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Organic Chemistry.

General Course—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d. An advanced course of lectures will also be given one day a week during the session. Fee, £2 2s.

Colloquium.

A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various departments of Chemistry. Students and others interested are invited to attend.

Practical Chemistry.—Laboratory Instruction.

The Chemical and Metallurgical Laboratories will be open daily from 9 a.m. to 5 p.m., except on Saturdays, when they are open to senior students only. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

Days per Week ..	Five.	Four.	Three.	Two.	One.
Per Session	15	12½	10	7½	5
,, Two Terms ..	11	9	7½	5½	3½
,, One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days. Special facilities are afforded for Research and Post-graduate work.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

Evening Lectures.

A course of Lectures dealing with the principles and theories of modern Chemistry will be delivered during the First and Second Terms. Fee, 10s. 6d.

Practical Chemistry—Laboratory Instruction.—The Laboratory will be open one evening a week from 6 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—Two Terms, 21s; One Term, 12s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at

which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Registrar.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.
Assistant Professor—Frederick W. Rixon, M.Sc., Ph.D.
Lecturers—H. A. M. Borland, A.R.C.S.; E. E. Elt, B Sc
Demonstrators—E. H. T. Parker; P. W. Alloway; C. D. Fuller.
Assistants in Chemical Laboratory—W. F. Phillips and C. Cox.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry and Analysis to Students of either sex. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture.

Special facilities will be given to Students wishing to undertake research work approved by the Professor; and the Courses provide for the Examinations in Chemistry for the B Sc., M.B., and D.Sc. degrees of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute.

The Laboratories are open every week-day from 9.30 till 12.30, and from 2 to 5 p.m., except Saturday, when they close at 12 30.

The Annual Fee of £10 10s. secures (in addition to the use of the Laboratory) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and Engineering Workshop.

The College Day Classes re-open on Sept. 17, and the Evening Classes commence on Monday, September 30.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (free).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D F.R.S., P.I.C.
Assistant Lecturers and Demonstrators—Alex. Findlay, M.A., D.Sc., Ph.D.; Hamilton McCombie, M.A., Ph.D., B.Sc., A.R.C.S., A.I.C.; C. K. Tinkler, B.Sc., and T. J. Murray, Ph.D.

The Session will be opened on October 1st, 1907.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. Mondays to Thursdays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9 30 to 10 30 a.m. Fee, £1 11s. 6d.

Second Year.—Advanced Organic Chemistry.—This course extends over two years, and is divided into two parts:—(*a*) Carbon Compounds of the Fatty Series; (*b*) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *General and Physical Chemistry.*—This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General and Physical Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6¼

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. GARDNER, M.Sc.

DEPARTMENT OF CHEMISTRY AND DYEING.

Professor of Chemistry and Dyeing—W. M. Gardner, M.Sc.
Assistant Professor of Chemistry—B. North, A.R.C.Sc. (Lond).
Lecturers in Chemistry—L. L. Lloyd, Ph.D.; S. F. Stell, F C.S.
Demonstrators in Chemistry—S. M. Sutcliffe, F.C.S.; S. R. Illingworth.
Lecturer in Physics—J. A. Tomkins, A.R.C.Sc. (Lond.).
Demonstrator in Physics—E. B. Walker.
Lecturers in Dyeing—A. Herz, Ph.D., and A. B. Knaggs F.C.S.
Demonstrator in Dyeing—L. Minikin.
Lecturer in Gas Manufacture—W. Cranfield.
Lecturer in Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided :—

I. *General Chemistry Course*, extending over four years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Extending over one or two years.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.), London.*—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D , B.Sc.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc , Ph.D.

Assistant Lecturer and Demonstrator—W. Lowson, B.Sc., F.I.C.

Demonstrators—W. H. Perkins, B.Sc.; H. Calam, M.Sc.; A. T. King, B.Sc ; J. Marshall, B.Sc.

The Session begins October 1, 1907.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Advanced Inorganic Chemistry.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Advanced Inorganic Chemistry.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Honours Courses.—(*a*) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon in the First and Second Terms; fee, £2 12s. 6d. (*b*) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £1 11s. 6d. (*c*) Physical Chemistry: Monday, Wednesday, and Friday at 9 30 a.m. in the Second and Third Terms; fee, £2 12s. 6d. (*d*) Electro-chemistry: One hour weekly; 31s. 6 l.

6. Chemistry of Food and Drugs —Special class for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £2 2s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from April to June. Fee, £5 5s.

Dyeing and Tinctorial Chemistry Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Chemist—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—A. B. Steven, B Sc.

Demonstrator—Ian Q Orchardson, B.Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, M.Sc., F.I.C.

Assistant Lecturer and Demonstrator—F. Kopecky.

Demonstrator—Harold Brumwell.

Research Assistant—H. G. Bennett, M.Sc.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture.

Fuel and Metallurgical Department.

Professor—William A. Bone, D.Sc., Ph.D , F.R.S.

The Courses extend over two, three, or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the microstructure, physical properties, and heat treatment of steel and other industrial alloys.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Chemistry—J. Campbell Brown, D.Sc.

Professor of Physical Chemistry—F. G. Donnan, M.A. Ph.D.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy — Guy D. Ricketts, M.A., A.R.S.M.

Demonstrators and Assistant Lecturers — A. T. de Mouilpied, M.Sc., Ph.D.; H. Bassett, B.Sc., Ph.D., D.es.Sc.; F. J. Brislee, D.Sc.; A. Rule, M.Sc., Ph.D.; E. Garratt, M.Sc.; and T. E. Gardner, B.A., B.Sc.

Assistant—H. H. Froysell.

The Session commences October 8th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £3.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £2 10s.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—History of Chemistry and Chemical Philosophy. Fee, £2.

Courses J.—Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Fuel and Gas. (6) Technical Gas Analysis.

Course K.—Applied Organic Chemistry.

Course L—Applied Electro-chemistry.

Fee (Courses J, K, L), three terms, £2 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis; preparation of Inorganic Compounds; simple Quantitative and Volumetric Analysis. (3) Revision Class. (4) Engineers' Class. (5) General Metallurgy (Elementary).

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water and Gas Analysis, Photometry and Photography, Electro-chemical Work, Metallurgy Laboratories, Research Laboratories and Library, and a Museum. Large new Laboratories for Physical Chemistry and Electro-chemistry have been recently erected.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

Per Week.	One Term, Three Months.	Three Terms One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

D.P.H. Course (see special syllabus).

Course for Dental Degree (see special syllabus).

Veterinary Course (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sir John Willox Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1907, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15. The Sheridan Muspratt Scholarship, on similar lines, will be open for competition in December, 1908. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes on Metallurgy and Physical Chemistry will be held during the winter.

Prospectuses containing particulars may be obtained from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—F. C. Garrett, D.Sc., F.C.S.

Assistant Lecturer and Demonstrator—J. A. Smythe, M.Sc., Ph.D.

Demonstrator—A. A. Hall, M.Sc., Ph.D.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant to Lecturer in Agricultural Chemistry—J. Watson, B Sc.

First Year Courses.—I. *General Course.*—This Course o Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 9 h. Fee, £3 10s. for the Session.

II. *Special Course.*—More advanced than the above. Wednesdays and Fridays, 11 to 12. Fee, £3 10s. for Session.

For Diploma in Electrical Engineering.—Tuesday, 12 to 1. A course of Lectures will be given dealing with the Principles of Chemistry, Fuel, the Phenomena of Combus-

tion, and Metals and Alloys employed in Engineering, &c. Fee for the course, £2.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 8th. The class for Inorganic Chemistry meets at 11 a.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Professor Louis, M.A., F.I.C., F.C.S.; Demonstrator, H. Dean, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £3 10s. per term, £9 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in the following subjects:—Arithmetic; English Essay; Geometry; the subject-matter of Euclid, Books I., II., III.; Algebra, up to and including Quadratic Equations. Also any two of the following:—English Language; Latin, including Grammar and Easy Sentences; Greek; French; German; Geography. The next examination commences on September 30. Names to be sent in at least ten days before this date. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—1. The first examination for the Degree of B.Litt. 2. Durham Examination for certificate of proficiency in General Education, held in March and September. 3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

The University has recently adopted the following Matriculation Examination for students entering the Faculty of Science:—Additional Mathematics; English; English History; any *one* subject selected from Religious Knowledge, Botany, Zoology, Physical and General Geography, Experimental Science; any *two* subjects selected from Latin, Greek, French, German. (Students may substitute Extra Mathematics for one of these optional subjects up to and including September, 1911).

In order to enter on a three years' course of study for a Degree in Letters a student must have previously satisfied the Examiners in the following subjects:—Elementary Mathematics or Additional Mathematics; English; English History; either Latin or Greek; either French or German; *one* of the following subjects—Religious Knowledge, Botany, Zoology, Physical and General Geography, Experimental Science.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—Every candidate for the Bachelorship in Science will be required to satisfy the examiners in Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the third year in an examination in one chief and two auxiliary subjects. For details of the subjects the College Calendar should be consulted. Candidates may qualify for the degree of B.Sc. by attending special courses in Agriculture, Engineering, and Mining, and passing the several examinations.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in September next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, October 3rd.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 30th. Candidates should send in their names to the Secretary on or before September 20th.

THE UNIVERSITY OF MANCHESTER.

Professor and Director of the Chemical Laboratories—Harold B. Dixon, M.A., M.Sc., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Senior Lecturers and Demonstrators—G. H. Bailey, D.Sc., Ph.D.; C. Weizmann, Ph.D.; Norman Smith, M.Sc.

Assistant Lecturers and Demonstrators—E. C. Edgar, D.Sc.; H. F. Coward, M.Sc; Ida Smedley, D.Sc.; and J. L. Simonsen, M.Sc.

Lecturer in Organic Chemistry—J. F. Thorpe, Ph.D.

Professor of Metallurgy—H. C. Carpenter, M.A., Ph.D.

Lecturer in Electro-Chemistry—R. S. Hutton, D.Sc.

The Session begins October 1, 1907.

The Chemical Classes form part of the Courses for Degrees in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during the Lent Term.

These courses are intended for Students commencing the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Metallurgy—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: Two hours per week during the Michaelmas Term.

Applied Electro-chemistry: One hour per week during Lent and Easter Terms. A course of six lectures on the Electric Furnace and its Applications will be given on Saturday afternoons during the Michaelmas Term.

Applied Chemistry.—(1). Sulphuric Acid and Alkali Manufactures; General Principles of Chemical Engineering. (2). The Natural and Artificial Colouring Matters and the Principles of Dyeing and Printing. (3). The Chemistry of Fuel.

Chemistry Laboratory Courses.

During the first year, the student works in the "Roscoe" or the "Dalton" Laboratory at Qualitative Analysis and Inorganic Preparations. Second Year Students work at Quantitative Analysis, and also take a Laboratory Course in Physics or some other subject. Third Year Students work in the "Schorlemmer" Laboratory of Organic Chemistry, and may also undertake experimental work in some special branch of Chemistry.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Metallurgical Laboratory.—This has been recently much enlarged and re equipped, mainly with a view to post-graduate work on the Structure of Metals and the Chemistry of Fuel.

Applied Organic Chemistry.—In connection with the "Schorlemmer" and "Schunck" Laboratories, a special laboratory is fitted with apparatus and appliances suitable for investigations on Dyes and other organic substances on a large scale.

Electro-chemical Laboratory.—In addition to such apparatus as is required for experimental work on Electrolysis and the Electro-deposition of Metals, special equipment is provided for investigations with the Electric Furnace.

Chemical Research.

In addition to the facilities mentioned above for Metallurgical and Electro-chemical Research, the following laboratories are available for post-graduate work:—(1) The private Laboratories of the two Professors; (2) The "Frankland" Laboratories for Physical Chemistry; (3) The "Schunck" Laboratory for Organic Chemistry; (4) The "Thorpe" Laboratory for Organic Chemistry.

To encourage post-graduate work of this kind, the University gives a "Beyer" Fellowship (£100 per annum) and Scholarships (£50 per annum).

The "Dalton" Chemical Scholarship (£50 per annum, tenable for two years) is also awarded, and the 1851 Exhibition Scholarships (£150) may be held in the Laboratory. Further, Honorary Research Fellowships and Research Studentships are granted from time to time to those who are capable of carrying out original investigations.

Two "Schunck" Research Assistants are appointed annually.

Courses for Degrees.

To qualify for the Ordinary Degree of B.Sc. Students have to attend a prescribed course of study extending over three years, and are recommended to pass the Matriculation Examination before entrance. (Subsequent to October, 1906, three years attendance *after* matriculation will be compulsory).

The course of the Degree of B.Sc. with Honours in Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); an additional course (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Physical or some other Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Lecture course in some Special Branch of Chemistry; History of Chemistry; Chemical Laboratory (5 days per week, for one of which attendance in another Laboratory may be substituted).

For the M.Sc. Degree post-graduate work is required. The D.Sc. may be obtained after four years from graduation, provided that the candidate has distinguished himself in research.

Certificate in Applied Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D Sc., F.I.C.; G. Sand, D.Sc.; and G. Martin, Ph.D, B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences October 7th, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. Evening students, 10s. for 2 hours per week, 3 hours 15s., 4 hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturers and Demonstrators—W. E. S. Turner, M.Sc., B.Sc.; W. J. Jarratd, B.Sc.; C. R. Young, B.Sc.

The Session will commence October 2nd.

Matriculation Course. — Tuesday and Friday at 9 30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, and Biology. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education.

Intermediate Course in Chemistry for B.Sc. or M.B.—Monday, Tuesday, Thursday, and Friday at 9 30 a.m. £5 5s., and nine hours per week Laboratory work.

B Sc. Course in Chemistry.—Tuesday and Wednesday at 5 p.m., with another hour to be arranged, £4 4s., and 12 hours per week Laboratory work during two Sessions.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon any Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five year's standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health will be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Board of Education, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lecture Class and Laboratory, on Wednesday evening during the Michaelmas and Lent terms. Fee, £1 10s.

Department of Metallurgy.

Professor of Metallurgy—J. O. Arnold. This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A new steel works has recently been erected in connection with the Sheffield College at a cost of about £10,000. The works include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works is also provided with a hammer capable of dealing with four-inch ingots Differential annealing furnaces, oil brightening and lead-tempering tanks will constitute part of the new plant. Additional laboratory accommodation is attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers—J. S. Lumsden, Ph.D., D.Sc., and J. K. Wood, D.Sc.

Lecture Assistant and Lab. Steward—J. Foggie, F.C.S.

The Winter Session begins early in October and ends in March. The Summer Session extends from the middle of April to the end of June.

The Junior Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

Chemistry.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—Francis W. Gray, M.A., B.Sc., and Joseph Knox, D.Sc.

I. *General Lecture Course* (100 *Lectures*),— Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic

Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. *Special Lecture Course on Organic Chemistry* (50 *Lectures*).—Daily during the Summer Session. Fee, £3 3s.

III. *Practical Course for Medical Students.*—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

IV. *Chemical Laboratory.*—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

V. *Physical and Advanced Inorganic Chemistry* (30 *Lectures*.—In connection with the Laboratory work, three Lectures a week on Physical Chemistry and selected portions of Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Mr. F. W. Gray. Fee, £2 2s.

UNIVERSITY OF ABERDEEN AND ABERDEEN AND NORTH OF SCOTLAND COLLEGE OF AGRICULTURE.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; W. J. Profeit, M.A., B.Sc.; and H. M. Will, M.A., B.Sc.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. *Agricultural Chemistry* (*General Course*).—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Laboratory.*—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; and W. W. Taylor, M.A., D.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. Advanced Courses of 25 lectures each are given in the Winter and Summer Sessions; fee, £1 1s. An Intermediate Course of Organic and Advanced Inorganic Chemistry is held in summer; fee, £2 2s. There is also a class on History of Chemistry or Chemical Theory, by Dr. Dobbin; fee £1 1s.: and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order). Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis), Physico-chemical Measurements, Agricultural Chemistry, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical Chemistry; Organic Chemistry; Physical Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by

himself:—Gas Analysis; Assaying; Physico-chemical Measurements, including Practical Crystallography as a special branch.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry *may be* required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.
Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—R. B. Denison, D.Sc., Ph.D.; Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.; E. B. R. Prideaux, M.A., D.Sc.

The Session begins October 1st, 1907.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electrochemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Students who have been three and four years in the Chemistry Department, arrangements have been made for their spending from four to twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory, under the charge of Dr. Emil Westergaard, has been provided for the study of Technical Mycology, including Brewing, Distilling, Malting, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Bread Making, Butter and Cheese Manufacture, &c.

Matriculation Fee, 5s.; Composition Fees from £12 12s. to £15 15s. Full particulars are published in the Calendar of the College, which is issued early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.
Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.
Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 23. Entrance Examination Sept. 16.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1907-1908 may be had from Mr. H. F. Stockdale, Secretary; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

United College of St. Leonard and St. Salvator.

Professor of Chemistry — T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 11th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about forty Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 28th and following days. Twenty-four of these Bursaries are restricted to Men, one to Men or Women, and fifteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Berry Research Scholarship in Chemistry, of the value of £80, tenable for one year, will be open to competition by students of either sex at the close of the Winter Session.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Examinations in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £5 5s.

A special Research Department has been instituted by the University, the laboratories of which are open to

students who give proof of their capacity of conducting chemical investigation.

QUEEN'S COLLEGE, BELFAST.

Professor— E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—John Taylor, M.Sc.

The College Session will commence on October 15th, 1907, and end on June 13th, 1908. All classes are open to male and female students.

The courses in Chemistry, though designed primarily to meet the requirements of candidates proceeding to the Examinations in Arts, Medicine, and Engineering of the Royal University of Ireland, of the Medical Licensing Bodies of Dublin and Edinburgh, and of the Pharmaceutical Society of Ireland, can be arranged specially as required, so as to render them suitable to any particular course of study. The following courses are provided:—

Systematic Chemistry.

I. General Lecture Course; three terms. Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.

II. Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.

III. Winter Course of Practical Analytical Chemistry; commencing early in January, 1908.

IV. Summer Course of three months' duration, for students of Medicine; ending about the third week in June.

V. Course for Pharmaceutical Students; held during the second and third terms.

Laboratory Work.

VI. The Chemical Laboratory is open daily from 10 to 4 o'clock, except on Saturdays, to Students entering for Special Courses of practical work in General Inorganic Chemistry, Qualitative and Quantitative Analysis, Organic Chemistry, or for the purpose of Original Investigation.

Scholarships, &c.—In addition to the Class Prizes given at the Sessional Examinations, the College awards a Senior Scholarship of the value of £40, for Chemistry and Physics (either of which may be taken as a limited course), and numerous Junior Scholarships in Arts, Medicine, and Engineering, of which chemistry forms a part, value from £20 to £24 each, annually. The Royal University of Ireland also offers Exhibitions in Chemistry and Physics, First-class value £42, and Second-class value £21, together with other prizes, *e.g.*, a Studentship of £100 per annum, tenable for three years; and the 1851 Exhibition Scholarships, value £150, tenable for two, and, under certain circumstances, for three years, have from time to time been placed at the disposal of the College.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c,, are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senier, Ph.D., M.D., F.I.C., F.C.S., M.R.I.A.

Demonstrator—Arthur Compton, B.A.

Research Assistant—Percy C. Austin, M.A.

The Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts. — 1. Second year's Course, Inorganic and Organic, and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts. — 1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.* — 1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.* —1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by five Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Dean of Faculty and Professor of Chemistry—W. N. Hartley, F.R.S., D.Sc.

Lecturer on Organic Chemistry—Alphonsus O'Farrelly, M.A.

Senior Assistant—J. Holms Pollok, D.Sc.

Junior Assistant—G. G. Leonard, A.R C.Sc.I.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships include free education for the full Associateseip Course of three years and maintenance allowance of a guinea a week during the Session.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

City and Guilds of London Institute for the Advancement of Technical Education.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds Central Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 17th, and the Winter Session opens on Tuesday, October 1st. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 17th. Session begins October 1st. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

City of London College, White Street, Moorfields.—I. S. Scarf, F.I.C., F.C.S., and Assistants. Courses of Saturday and Evening Lectures and Laboratory Practice in Chemistry and Physics, open to Students of both sexes. Day Commercial School, commences Sept. 16. Session commences September 30th.

Battersea Polytechnic.—Principal, Mr. S. G. Rawson, F.I.C. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), assisted by Mr. John L. White, D.Sc., Mr. J. Hart Smith, A.R.C.Sc., F.I.C., and others. Session opens Sept. 30. Complete courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Paper and Pulp Testing, Paper Making, Gas Analysis, Assaying, Oils, Fats, Soap and Candle Manufacture.

Birkbeck College, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. Alex. McKenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. This Institution, which has now completed eighty-four years of educational work, will commence the new Session on Monday, September 30, when G. G. Chisholm, Esq., M.A., B.Sc., will give the Opening Address, at 7.30 p.m. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, and various branches of Law. Courses conducted by recognised teachers of the University provide for the Examinations of the University of London, in the faculties of Arts, Science, Commerce, and Law. The Report for the last session shows that during the year 104 students passed some examination of the University of London, while a large number gained successes at various public examinations. The College has added considerably to its appliances in recent years, and the Physical, Chemical, Biological, and Metallurgical laboratories are very thoroughly equipped. Courses in Mining, Metallurgy, and Assaying are given both in the day and evening. The Modern Language classes include Italian and Spanish, as well as French and German. The College possesses a School of Art, open both day and evening. The Calendar supplies detailed information respecting the Courses of Study, Examinations, Studentships, &c.

Borough Polytechnic Institute, 103, Borough Road, S.E. — Chemistry: Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry (Session fees, per course, 10s. to 15s.); Electrochemistry,

lecture on Wednesday evenings; Dr. F. Mollwo Perkin, assisted by H D. Law, B.Sc., and C. T. Bennett, B.Sc Electricity and Magnetism, and Electro-technics: Evening Lectures and Laboratory Work (Session fees, per course, 10s. to 15s.), Dr. J. Henderson, assisted by H. Saunders. Special Evening Courses on Painters' Oils, Colours, and Varnishes. Session opens Monday, Sept. 23.

South Western Polytechnic, Chelsea, S.W.—Principal, Sidney Skinner, M.A. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, Photography, &c. Systematic Courses are held for the Matriculation, Inter. Sci., and B.Sc. Examinations (Pass and Honours) of the University of London. The Day Course in Chemistry is of three years' duration; it gives a thorough training to those who wish to become Consulting or Industrial Chemists. Prospectus of Day and Evening Classes may be obtained from the Secretary, 1d., by post 4d.

East London College, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Assistants, Clarence Smith, D.Sc., and F. G. Pope, B.Sc. Lectures and Practical Classes are conducted in the Day Technical College, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination, B.Sc. (Honours and Pass). Special attention is given to work for the Honours Examination and research. Evening Classes for London University Degrees are also held. The College re-opens October 1st.

University Tutorial College, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

Sir John Cass Technical Institute, Jewry Street, Aldgate.—Principal, Charles A. Keane, M.Sc., Ph.D., &c., assisted by H. Burrows, Ph.D., F.I.C., Arthur R. Ling, F.I.C., R.S. Willows, D.Sc., and C. O. Bannister, A.R.S.M. Evening Classes in Chemistry, Metallurgy, Brewing and Malting, Physics, and Mathematics, designed to meet the requirements of those engaged in Chemical, Metallurgical, and Electrical industries, and also in other departments of Science and Art. Practical laboratory work. Courses of Instruction in Glass Blowing, by A. C. Cossor. Classes begin September 23. Full details may be obtained on application, or by letter to the Principal.

The Institute of Chemistry of Great Britain and Ireland.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, (i.) to promote the better education of persons desirous of becoming public and technical analysts and chemical advisers on scientific subjects; (ii.) to examine Candidates, and to grant certificates of competency; and (iii.) to elevate the profession of Consulting and Analytical Chemistry by setting up a high standard of scientific and practical proficiency and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University approved by the Council, or in the laboratory of a Fellow of the Institute, with the object of adopting the profession of Analytical and Consulting Chemistry. *The Intermediate Examination.*—Candidates for admission to the Intermediate Examination are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Advanced Mathematics; (ii.) Mechanics and Chemical Engineering; (iii.) Metallurgy; (iv.) Geology and Mineralogy; (v.) Physiology; (vi.) Bacteriology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' training in a recognised Institution as indicated above, and work systematically for two other years in the laboratory of a Fellow of the Institute. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also passed in at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. *The Final Examination for the Associateship (A.I.C.).*—Any Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *Fellowship (F.I.C.).*—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of Applied Chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (Price One Shilling) of Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C.

Imperial College of Chemistry and Pharmacy, 49 and 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction is given at this College in Pharmacology and Therapeutics, *re* the Institute of Chemistry Examination. Students attending the College visit technical works.

The Polytechnic, 309, Regent Street, W.—University of London Preparation Classes. Chemistry: R. A. Ward, F. E. Weston, B.Sc., F. Harvey, W. H. Collier, and H. R. Ellis, B.Sc.

Blackburn Municipal Technical School.—Chemistry: Mr. Robert H. Pickard, D.Sc.(Lond.), &c., assisted by Messrs. Jos. Yates, W. O. Littlebury, F.I.C., and Jos. Kenyon. Session opens Monday, Sept. 23. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d).

Redruth School of Mines, Cornwall.—Principal, Howard C. Ridding, A.R.S.M., F.I.C., assisted by a staff of Mining Engineers and Mine Surveyors. Courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Shorter Courses are also held in the above-named and cognate subjects to meet the requirements of those having a limited time at their disposal and Prospectors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application to the Registrar. Session commences Wednesday, Sept. 11.

County Technical Laboratories, Chelmsford.—Agriculture: B. W. Bull, N.D.A. Analyst: V. H. Kirkham, B.Sc., A.I.C. Biology: C. A. Ealand, B.A., R. Robson,

B.Sc. Chemistry and Physics: A. Neville, B.Sc., A.I.C., H. T. Cranfield, Miss K. Jackson.

Leeds Institute: Technical School, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in over sixty subjects of Science and Technology, among which are:—Chemistry (Inorganic and Organic), Chemical Calculations and Principles of Analysis, by Mr. R. E. Barnett, B.Sc., A.R.C.S., Mr. J. B. Murray, Mr. A. McFarlane, and Mr. O. F. Kirby, M.A., B.Sc.; Metallurgy (Theoretical and Practical) and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Gas Manufacture, by Mr. W. E. Pettigrew; Oils and Fats, by M. W. Dillon; Magnetism and Electricity, Practical Physics, &c., by Mr. J. E. Tindall, B.A., B.Sc.; Botany, Lectures and Practical Work, by Mr. N. Walker; Photography, by Mr. S. E. Bottomley. Fees: from 7s. 6d. per session. Group courses arranged for Students engaged in Chemical Industries Session commences Sept. 17th. Prospectuses of various Classes free on application to the Head Master, or to Mr. James Graham, Secretary for Higher Education, Calverley Street, Leeds.

City of Leeds Higher Education Department.—Courses of Evening Classes have been arranged for the Minor Examination of the Pharmaceutical Society, in which the whole Syllabus will be covered in three Winter Sessions. Chemistry: Mr. S. Parrish, B.Sc., A.R.C.S., Chief Lecturer in Chemistry, Central High School, and Mr. J. B. Murray. Botany: Mr. Norman Walker, Assistant Lecturer in Botany, Leeds University. Pharmaceutics: Mr. J. H. Gough, Ph.C., F.C.S., Demonstrator in Materia Medica and Pharmacy, Leeds University. Full particulars from Mr. James Graham, Secretary for Higher Education, Education Offices, Leeds.

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Errata.—P. 98, col. 1, line 3 from bottom *read* "reference and free from hypothesis." P. 107, col. 2, line 33 from bottom, *for* "Borides" *read* "Bromides."

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THE ATOMIC WEIGHT OF RADIUM.

By Mdme. CURIE.

The determination of the atomic weight of radium which I published in 1902 (*Comptes Rendus*, July, 1902) was carried out with 9 centigrms. of radium chloride. Fresh processes having since then furnished some decigrms. of practically pure chloride, I have subjected them to purification, which enabled me to obtain 4 decigrms. of perfectly pure radium chloride, and to determine the atomic weight of radium under far better conditions than before.

[Note.—I have already had an opportunity of thanking those who, in the first years of our researches on radio-active substances, gave the assistance which is indispensable in such costly experimental work (Mdme. Curie, Thèse de Doctorate). I am glad to take this opportunity of thanking those who have now enabled me to obtain a relatively large amount of radium salt. The best radium mineral (the residue of Joachimsthal pitchblende after the extraction of the uranium) being in great demand, the Austrian Government, at the suggestion of the Vienna Academy, has consented to reserve to us the right of buying 10 tons of this mineral. Baron E. de Rothschild has kindly provided the funds necessary for buying this amount. Finally, the treatment of this mineral has been, and is still being, carried out at the factory of M. Armet de Lisle, who has most generously defrayed the cost, and who has also kindly allowed us to make use of his factory for studying radio-active substances.]

The purification processes consisted as before in fractional crystallisation in water containing hydrochloric acid, or in fractional precipitation of the aqueous solution by alcohol. The progress of the fractionation was controlled by photographs of the spark spectra, obtained with the spectrograph which formerly belonged to Demarçay. It is convenient to compare the relative values of the lines 4554·4 of barium and 4533·5 of radium. These lines, which are very close together, are very suitable for comparison. The line 4554·4 is the strongest in the barium spectrum, and the line 4533·5 is one of medium importance in the radium spectrum.

When the purification was stopped, the strongest barium line was still faintly visible near the other. Its complete elimination seemed to be very difficult with the quantity of material I had at my disposal. Nevertheless, I shall shortly show that the salt was very pure.

I was confronted with one difficulty during this work. When a clear solution of a radium salt is evaporated in a dish or glass, the dry salt obtained is not generally completely soluble in water, but leaves a residue. I have found that this residue is partly due to the formation of radium sulphate, in consequence of the presence of traces of sulphuric acid in the reagents (traces which could only be detected by barium salts after the concentration of the reagents), and partly to the slow action of the radium salts on the vessels. I therefore decided to prepare specially all the reagents employed. The water was distilled in a platinum still, and received and kept in a platinum flask; this water was used to prepare the hydrochloric acid, which was also kept in a platinum flask. The nitric acid, alcohol, and silver nitrate were also purified. It is not possible to let the radium chloride crystallise in presence of hydrochloric acid in a platinum dish, because it has considerable action on the latter. But if the clear solution is allowed to crystallise rapidly in a porcelain dish, crystals are obtained, which, after being dried, dissolve in the purified water without residue, and hence can be used to determine the atomic weight.

The method employed for this determination was the same as before. It consists in estimating as silver chloride the chlorine contained in a known weight of anhydrous radium chloride. According to my earlier experiments, which were confirmed by new observations, radium chloride, which has just been prepared, loses its water of crystallisation when it is heated in a drying oven above 100°, and its weight is quite constant when it has been subjected for half-an-hour to a temperature of 150°.

The weighings were performed with a Curie's aperiodic balance with direct reading for weights below decigrms. This rapid balance is accurate to one-tenth of a m.grm., and takes only ten seconds to reach its position of equilibrium. The weighing of the radium chloride is more difficult than that of the silver chloride, because the former salt absorbs water-vapour rather quickly; it is therefore essential to let it cool in a desiccator with phosphoric anhydride before weighing, and not to re-commence weighing until after it has been again placed in the drying oven, even if the cage of the balance contains desiccating substances.

After each estimation the radium is present as nitrate with silver nitrate. The silver is eliminated by hydrochloric acid, and the nitric acid by repeated crystallisation in presence of hydrochloric acid.

The following table gives the numbers obtained in three consecutive experiments, and the atomic weights P deduced from them, assuming that radium is a divalent metal, and that the atomic weights of silver and chlorine are—

$$Ag = 107{\cdot}8,\ Cl = 35{\cdot}4.$$

Radium chloride.	Silver chloride.	P.
0·4052	0·3906—0·00006	226·35
0·4020	0·3879—0·00006	226·04
0·39335	0·3795—0·00006	226·15

Weight of filter ash = 0·00006.

The weighings of the two chlorides are considered to be exact to about one-tenth mgrm. These three experiments, which agree very closely, give for the atomic weight of radium the mean value 226·18.

The experiments, performed in 1902 with very pure radium chloride, gave less concordant results and a mean of 225. The spectrum of the salt used recently shows a rather greater degree of purity, but the difference of about one unit in the atomic weight could not be ascribed to this cause. I performed a control experiment as follows:—I prepared a solution of some mgrms. of pure 1907 salt, and added to it a small quantity of a titrated solution of barium chloride. The amount of barium salt in the mixture was 0·61 per cent. In the spectrum of this salt a great increase of the intensity of the barium spectrum is shown, whereas the change of atomic weight, calculated from the known addition of barium chloride, is only 0·7 unit. From the examination of the spectra it is clear that the difference between the numbers obtained in 1902 and in 1907 should be attributed only to the inferior accuracy of the experiments performed with only 9 centigrms. of radium salt and with less pure reagents.

The above experiment also proves that the spectral reaction of barium in presence of radium is very sensitive, and that the radium chloride which was used for the determination must be very pure. It certainly does not contain 0·1 per cent of barium chloride.

I therefore conclude from these experiments that the atomic weight of radium is 226·2 (Ag = 107·8, Cl = 35·4) with a probable error of less than half a unit.

If the values Ag = 107·93, Cl = 35·45 are adopted, the value is Ra = 226·45.

The reproduction of the spectra and the description of the details of the experiments will appear in the journal *Le Radium*.—*Comptes Rendus*, 1907, vol. cxlv., p. 422.

VALENCY.*

By A. WERNER.

Introduction.

THE development of the doctrine of valency shows that our present ideas of valency have resulted from the endeavour to obtain a numerical expression for those intramolecular affinity relations which, on the basis of chemical reactions, are to be regarded as the cause of the linking together of the atoms in the molecule. Thus, we must take as the basis of our conceptions of valency those structural and constitutional formulæ in which the affinity relations between the atoms are represented graphically by strokes. The number of the strokes in each case shows with how many other atoms the atom of any given element exists in so-called chemical combination, and thus determines the combining value of the atoms. This combining value is also called the valency of the elements. The valency was first regarded as a number of constant magnitude, characteristic of the atom of each element, and it was said to show with how many other elementary atoms it could combine. This view had, however, to be abandoned, for reasons to which I shall return later, and it was then thought that valency is a relative number depending upon the nature of all the atoms in combination with one another. Thus the idea of valency lost its original precise form, for owing to the great number of elements there were so many possibilities of combination for each atom that the valency of the atoms of an element could be represented by very different numbers. The chief object of the idea of valency—to afford a more settled basis for the representation of constitutional formulæ—was in consequence lost sight of. In order to preserve as much as possible of the original conception of valency, which had been so very fruitful in the region of the carbon compounds, in which it had chiefly been developed, for ten years attempts were made to compress the constitutional and structural formulæ of all possible compounds into schemes which could in no way fit in with the properties of the compounds. But, finally, it had to be recognised that in this way a corresponding doctrine of the constitution of the inorganic compounds could not be deduced, and hence the final result of these efforts is that the doctrine of valency has been confirmed for the compounds of carbon, but not for those of other elements. In consequence we were obliged to deduce the affinity relations in the molecules of compounds of other elements only from the properties of the compounds in question, paying no regard to the original ideas of valency, and to represent them graphically by suitable structural formulæ. Hence, it appeared that most elements can exhibit atomic linkages which could not be foreseen from the ordinary ideas of valency, and for which no theoretical expression could be deduced from these views. As a consequence, there necessarily arose the need of a comprehensive expression for the linkage power of the atom, a theoretical expression from which those constitutional formulæ which were based upon experimental work, but which could not be explained by the ordinary valency ormulæ, could be deduced. The doctrine of valency is in this state of development at the present time, and recent efforts in this region can therefore be summarised by saying that a search is being made for a general law expressing all the possibilities of linking of the atom.

Recent Attempts in the Region of the Doctrine of Valency.

The final form of this general law is yet to be found, and the great difficulties which oppose the deduction of it in purely chemical ways show at once why we have tried to arrive at the formulation of this general law on another basis than that of the frequently very tedious investigation of constitution. Thus, you know that Abegg, from considerations which he bases upon a special form of the Periodic System of the elements, has tried to construct a general valency law of the elements. And undoubtedly the chemical valency theories which W. Barlow and W. J. Pope have developed from their views on the structure of crystal molecules are also to be regarded from this point of view. All these experiments are of great value, and will certainly help towards the explanation of the problem of valency. I shall now turn my attention to the purely chemical constitutional formulæ and the ideas of valency arising from them.

General Doctrine of Valency.

All the ideas of valency deducible from the experimentally established constitutional formulæ of organic and inorganic compounds can be called the "extended valency theory" as distinguished from those specially deduced from the constitution of organic compounds. At the present time this theory is not simple in character, but it is composed of different heterogeneous views, the internal fusion of which to comprehensive ideas may be regarded as the final aim of the investigation of valency. We shall now proceed to examine into these separate ideas.

a. Direct and Indirect Linkage.—It was formerly generally assumed that two atoms could be connected with one another by chemical affinity only if they were spacially close to one another, *i.e.*, directly bound to one another as it was called. On the ground of recent researches on the constitution of certain groups of inorganic compounds, viz., the metal ammonium compounds and hydrates, it has, however, been found that atoms can be connected with one another by chemical affinity if, in consequence of the interposition of definite atomic groups bound with the atom in question, a spacial juxtaposition is, as it were, mechanically prevented. This is the case with the compounds $[Co(NH_3)_6]Cl_3$, $[Co(OH_2)_6]Cl_3$, &c. In such compounds the ammonia and water molecules form, as it were, an envelope round the central metallic atom, and thus prevent the direct binding of the chlorine atom to it. This kind of atomic linkage we call "indirect linkage." Indirectly bound atoms and groups are distinguished from those directly bound usually by their much greater power of entering into reactions. This may be recognised in the chemistry of the compounds by the fact that these indirectly bound groups can be directly detected in the aqueous solution of the compounds by means of analytical reagents, while this is not the case with directly bound atoms. Thus, there exists a characteristic difference in the behaviour of directly and indirectly bound radicals, which may be demonstrated very strikingly in those cases in which the molecule of the compound contains both directly and indirectly bound groups. This is the case, for example, in the following compounds:—

$$\left[\mathrm{Co}^{\mathrm{Cl}}_{(\mathrm{NH_3})_5}\right]\mathrm{Cl_2} \text{ and } \left[\mathrm{Pt}^{\mathrm{Cl_2}}_{(\mathrm{NH_3})_4}\right]\mathrm{Cl_2}.$$

Thus, in the freshly prepared aqueous solution of chloropentammino cobalt chloride it has been found that two-thirds of the chlorine is instantaneously precipitated as silver chloride by silver nitrate, while one-third does not give this reaction. Hence, it must be concluded that indirectly bound groups possess the property of appearing as independent ions in aqueous solution, so that this kind of linkage may be called "ionogenic linkage." Groups which are not bound ionogenically even in aqueous solution remain united in complex radicals with the elementary atom to which they are attached, and then appear as complex ions. The difference between directly and indirectly bound groups is of fundamental importance in the consideration of the constitution of inorganic compounds, which is indicated by the fact that the development of the inorganic constitution doctrine already shows that both different kinds of linkages probably appear in all elements. The importance of this difference for the doctrine of valency lies chiefly in the fact that it leads to the following questions, which are independent of one another:—

* Paper forming part of a Discussion on this subject at the Leicester Meeting of the British Association (Section B), 1907.

1. How many atoms can be directly bound with a definite elementary atom?

2. How many atoms and groups can generally be attached to an elementary atom by chemical affinity?

We shall now consider these questions. The first leads to the conception of the co-ordination number, the second to that of valency.

1. *The Co-ordination Number.*

The investigation of the composition and behaviour of an exceedingly large number of compounds has led to the noteworthy result that the maximum number of atoms and groups directly bound with a central atom is in most elements equal to six, and in a small group of elements it is equal to four. Hence, it follows that the power of linkage of the ordinary atom, in so far as direct bindings are concerned, does not exceed a definite limiting value. This limiting value must therefore be regarded as an important fundamental property of the elementary atoms; it is called the co-ordination number. The co-ordination number is thus that number which states the maximum number of atoms with which a definite elementary atom can be directly linked. The co-ordination number for boron, carbon, and nitrogen is four, and for most other elements, including all the heavy metals, &c., it equals six.

From the fact that only a few elements of the first period, and specially those with the smallest atomic volume, possess the lower co-ordination number four, while all others whose co-ordination number can be determined have the same value six, it must be concluded that this number must be independent within wide limits of the affinity value of the elementary atoms. If, however, this is the case, the co-ordination number can be conceived only as a space number, and it is then that number which states how many atoms can be attached to an elementary atom in a first sphere. This conception leads to many deductions which can be established by experiment. Firstly, it is to be emphasised that with the carbon atom, of which the co-ordination number is four, the four groups, according to the hypothesis of van 't Hoff and Le Bel, are symmetrically disposed round it in space. A further confirmation is obtained from the fact that the saturated carbon compounds differ characteristically from the corresponding compounds of other elements in that they are incapable of forming complex compounds by the addition of other molecular components. Thus, carbon tetrachloride forms no chloro salts.

In the elements with the co-ordination number six the symmetrical space position is represented by an opposite arrangement at the angles of an octohedron. This octohedral position leads us to expect for the cases in which the six groups are not identical, *e.g.*, for molecular complexes, two spacially different possible positions, which must manifest themselves as stereoisomers of the compounds in question. This important conclusion has also been experimentally confirmed for three different elements, platinum, cobalt, and chromium. If we therefore regard the co-ordination number as a space number of the atom, very weighty reasons argue in favour of it, and the co-ordination number represents the first sharply defined theoretical expression, which discloses something definite about the linkage power of the atom. But the co-ordination number is also practically of great fruitfulness as a working hypothesis because it allows us to foretell, in compounds in which the co-ordination number of the central atom is not filled up, that by choosing suitable components co-ordinatively saturated types of compounds must be able to be prepared.

The Doctrine of Valency.

a. The Unit of Valency.—The original view of the cause of the possible intramolecular dependence between two atoms which we call chemical combination was that for each atom a definite number of unalterable single forces (units of valency) must exist, and that the linking between the atoms in consequence of the mutual saturation of these valencies occurs in such a way that each valency of one atom saturates one valency of the other. As now the hydrogen atom in the compounds considered always combined with only one other elementary atom, the hypothesis was put forward that hydrogen generally possesses only one unit of valency. Therefore it was called monovalent, and all elementary atoms or atomic groups which in chemical compounds take the place of one hydrogen atom, were said to be equivalent to it, *i.e.*, monovalent also. Atoms or groups of atoms which replace two atoms of hydrogen are divalent, &c.

This system of valency has been of great service; nevertheless, it no longer satisfies the demands now made upon a comprehensive system of valency. Thus, it takes no account of the fact that in an exceedingly large number of cases certain atoms are not capable of forming linkages with the hydrogen atom, or atoms and groups equivalent to it, but yet can form a whole series of other perfectly stable atomic compounds. For the valencies which produce these last atomic linkages the valency system based upon the valency of hydrogen can give no standard of comparison, and these new valencies were therefore called by a special name. The valencies referred to that of hydrogen were called principal valencies, and those not thus measurable auxiliary valencies. Thus, it was only because the originally used standard of valency, that of hydrogen, could not be applied as the basis of a system of valency including all atomic linkages that this artificial distinction was proposed. The distinction is not based upon the nature of the atomic linkages produced by the different valencies. This is shown by the fact that radicals united to one another by auxiliary valencies are often very much more firmly bound than those held together by principal valencies, so that no constant difference can be demonstrated as regards the stability of the compounds produced by principal and auxiliary bonds.

In many cases it is also quite impossible to decide whether a certain linkage is to be called a principal or auxiliary valency linkage. Two examples will be sufficient to show this, sodium nitroprusside and carbonyl potassium ferrocyanide:—

$$\left[Fe^{NO}_{(CN)_5} \right] Na_2 \text{ and } \left[Fe^{CO}_{(CN)_5} \right] K_3.*$$

It can hardly be stated by which kind of valency the NO and CO groups of these compounds are bound to the iron, chiefly because, as we shall soon see, the question in such cases is much too indefinite.

For purely structural purposes, *i.e.*, for the graphic representation of the atomic linkages, which are to be assumed on the grounds of chemical properties, the distinction between principal and auxiliary valencies is therefore of no significance, and it would be most natural if without distinction we always expressed all linkages simply by a dot or a stroke between the two atoms in question. If, however, the distinction between principal and auxiliary bonds and principal and auxiliary valencies is kept up, it is because it seems necessary, in view of the present transition state of the doctrine of valency, to construct sharply defined partial conceptions which can afterwards serve as the foundation stones of a more comprehensive conception of valency. When therefore it is required to mark a difference between principal and auxiliary bonds it is preferable to denote the first by a line and the second by a dot.

b. The Unit of Valency as an Unalterable Single Force.—Even now the hypothesis that the unit valency is an unalterable single force acting on the atom has many adherents, especially amongst purely organic chemists. This hypothesis has been extended, and the further assumption made that the single force acts at perfectly definite places on the surface of the atom and in definite directions in space. These hypotheses have, however,

* Written $\left[Co^{NO}_{(CN)_5} \right] Na_2$ and $\left[Co^{CO}_{(CN)_5} \right] K_3$, which is obviously a mistake.—*Ed.* C.N.

proved completely unfruitful, and in the region in which they have been more fully worked out, namely, that of the carbon compounds, it has been found that they do not agree with the actual phenomena. To show this from the experimental material would lead us too far to-day. It will be sufficient to remark that the phenomenon of change of valency, the process of racemisation in optically active compounds, the phenomena of transmutation in geometrically isomeric carbon compounds, and, moreover, the behaviour of carbon compounds with one or more so-called double bonds, are either not compatible with these hypotheses, or else can only be made to fit in with it by great straining. For many of these processes these hypothetical conceptions have led to the elaboration of such artificial schemes in the formulations that the unbiassed theoretical explanation of the experimental results has been very detrimentally influenced, and new hypotheses have constantly had to be brought forward to explain the facts. All these reasons must necessarily lead to the abandonment of the hypothesis of the valency unit as a definite individual force.

c. The Valency Number.—According to the original definition the valency number is the property belonging to the atoms of uniting with a definite unalterable number of the atoms of other elements. Kekulé conceived of the valency number in this sense.

Although this conception has the merit of being simple it has, nevertheless, proved untenable. The valencies of the elements have not constant but varying numerical values, and the true nature of valency phenomena will not be understood until a more accurate investigation of the change of valency has proved what factors influence the valency number. We must regard the nature of the elementary atoms bound with one another as the principal factor which determines the change of valency, for it appears that the atom of an element has a different valency according to the nature of the atoms of other elements linked with it. Hence, the important result follows that valency is not a property belonging to the atoms as such, but a relative property which is dependent upon the nature of all the atoms bound with one another. It is further to be noted that very often an element can combine with another in different proportions, *e.g.*, $FeCl_2$, $FeCl_3$, $SnCl_2$, $SnCl_4$, &c. As now the assumption formerly made to explain these different proportions, of a mutual binding of the atoms of the metal, is untenable, on the basis of the molecular magnitude of the compounds in solution, we must admit that an element can exhibit a changing valency towards another definite element. Also the valency appears to vary with the change of definite external factors, such as temperature, pressure, &c., but we cannot discuss these conditions now. An allusion must, however, be made to a phenomenon which is of considerable importance in the consideration of valency relations, namely, the fact that the change of valency is not equally strongly marked in all elements, but in strongly electro-positive elements, the metals, and in strongly electro-negative, the metalloids, appears most marked, and is exhibited only relatively seldom by electro-neutral elements, such as carbon. Enough has been said to show that the valency relations of the elements are very various, and that hence it would be difficult to regard them all from one general point of view.

The first attempt in this direction, described below, will therefore necessarily be incomplete. But it is hoped that it will show that a solution of the problem is possible.

Development of the Doctrine of Valency from a Single Fundamental Conception of Affinity.

a. Fundamental Hypothesis concerning Affinity.—As the basis for our examination we shall use the assumption that the affinity of the atom does not act in the form of a single definite force, but acts uniformly from the centre towards the surface of the atom. We do not employ hypotheses concerning the shape of the atom, for as the atoms, even in the molecule, must be assumed to be in constant motion, the exact form of them can be of only subordinate importance as compared with the limits of space in which these movements are completed. These space boundaries for simplicity sake we can regard as spheres, and hence in all developments work on the assumption that the atoms are spherical. But this assumption is not necessary for our examination, for we use no hypothesis about the form of the atom for the development of our theory. The assumption has, however, the advantage of making the mechanical picture of the structure of the molecule easier to conceive. Let us now proceed to consider the phenomena of valency in the light of the hypothesis, worked out by us, on the mode of action of affinity.

b. The Affinity Value of the Unit of Valency.—Each elementary atom is characterised by the definite amount of potential energy it contains, of which a certain amount can take effect as chemical affinity, if it encounters another atom. But this amount can vary within wide limits, for it is always dependent upon the nature of the atoms uniting with one another, or, as it is ordinarily expressed, upon the greater or smaller affinity of the elements in question for one another. Each atomic linkage is therefore characterised by the saturation of a definite amount of affinity, the absolute value of which changes in different cases and is dependent upon the nature of all the atoms present in the molecule. The determination of the absolute value of the linking power of the single bonds is at present not within the regions of possibility. At the most, from the behaviour of the compounds, we are enabled to form opinions whether in definite cases the affinity value of the linkages in question is greater or less. These opinions are based on the following considerations:—Usually if a large amount of the affinity contained by an atom has been used, it has at its disposal only a smaller amount of affinity than when this is not the case. Thus, for example, the oxygen atom of the water molecule, H_2O, has less affinity for further atomic linkages than the oxygen atom of the hydroxyl group. And, further, we can generally conclude that the atoms of the elements in atomic combinations which appear as independent molecules, in new atomic compounds will have smaller amounts of affinity to be saturated than in radicals which have no independent existence. As now the atoms of the first kind in the formation of new atomic linkages call into action auxiliary valencies, and those of the last kind principal valencies, we come to the conclusion that the auxiliary valency linkage corresponds to the saturation of a smaller amount of affinity than the principal valency bond. Thus, between principal and auxiliary valencies there exists a gradual difference as regards their affinity value, and the most varied transition steps will be possible between the two. Accordingly, a sharp line of demarcation between principal and auxiliary valencies cannot be drawn. The views developed above on the affinity value of atomic bonds lead to many interesting conclusions which we shall now discuss somewhat more fully.

1. *Electro-compounds.*—Closely connected with the difference in the affinity values of principal and auxiliary valencies is the power of the atoms of elements to form electro-compounds, among which we understand the so-called ionic condition of atoms and radicals. From a chemical valency point of view the electron shows itself to be equivalent to one atom of hydrogen, *i.e.*, it is monovalent. This means that to link an electron to the atom of an element an amount of affinity is necessary of that order of magnitude which corresponds approximately to the formation of a principal valency bond. Regarded from this point of view the ions appear simply as a special case of a chemical compound produced by the so-called principal valency.

2. *The So-called Double Bond.*—We cannot state anything about the maximum amount of affinity which can be used up between two atoms bound together. It seems probable that the amount of affinity satisfied must be greater the greater the amount still at the disposal of the

atom. Hence, if we compare the union of two groups CH_3 with that of two groups CH_2, the two carbon atoms uniting in the second case will saturate a much greater amount of affinity than in the first case. But in no case need the amount saturated by the carbon atom of CH_2 be double that saturated by the carbon atom of CH_3. Hence we obtain a conception of the so-called double bond. This represents a greater amount of affinity than the single, but does not reach the amount of two single carbon bonds. Still unsaturated amounts of affinity are at the disposal of the carbon atoms of the ethylene groups, which causes the well known transformation phenomena of the ethylene bonds, and as these unsaturated amounts of affinity will be at the same time dependent on the nature of the atoms and radicals linked to the carbon atoms, the unsaturated character of the ethylene compounds must be able to vary within wide limits. This is actually the case, as a comparison of tetraphenyl ethylene, ethylene, and fulvenene shows at once. Many other deductions can be made from the consideration of the changing affinity value of the atomic linkages, but it would require more time than is now at our disposal to go into them fully. We shall therefore content ourselves with discussing shortly the question how the valency numbers can be deduced with the aid of our fundamental views on affinity.

c. Deduction of the Valency Numbers from the Fundamental Hypothesis.—According to our fundamental view, a part of the affinity contained by the atom is saturated by each atomic linkage. The number of the atomic linkages which can be formed will therefore be dependent, on the one hand, on the amount of affinity contained in the atom, and, on the other, on the amounts of affinity which have been saturated by linkages. The ratio of these two to one another will determine the valency number. Hence, we must turn to the questions of the amount of affinity contained in the atom and the magnitude of the affinity value of the linkages of the atom.

1. *The Affinity contained in the Atom.*—There can naturally be no question of a determination of the absolute value of the affinity contained in the atom. We must limit ourselves to trying to find out whether the amount of affinity contained by all atoms is the same, or is different with different elements. For this purpose we shall be obliged to determine the power of combination of an element which behaves itself as uniformly as possible towards others, *i.e.*, requires about equal amounts of affinity when forming an atomic linkage. Hydrogen is suitable for this purpose, for it behaves towards the metalloids as a positive element and towards positive elements as a negative element in hydrides, and occupies a mean position with regard to elements with a feebly defined character (carbon, &c.). If now we compare the composition of hydrogen compounds in the different periods of the natural system of the elements, we arrive at the result that the affinity contained in the atom of an element reaches a maximum in the elements which occupy the middle position (carbon), and decreases according to a law towards the electro-chemically strongly defined elements. The periodicity of the valency numbers of the elements for hydrogen is thus to be regarded as a consequence of the different amounts of affinity contained in the atoms, and the corresponding phenomena in regard to the alkyl compounds are to be ascribed to the same cause. The valency relations resulting from the composition of compounds with distinctly positive or negative elements are to be regarded quite differently. In these cases the affinity values of the atomic linkages, which vary within wide limits, play a great part, as I shall now try to show.

2. *The varying Affinity Value of the Linkages of the Atom as a Cause of the Valency Number.*—Carbon as regards its character takes a middle position between the metals and the metalloids, like hydrogen, and hence it behaves uniformly towards both groups of elements. This analogy explains why the valency numbers of most elements for carbon harmonise with those of the elements for hydrogen, and also why there is a far-reaching agreement between the valency of carbon for hydrogen and that for other elements. But these simple relations in valency phenomena carbon owes only to its peculiar position as regards the other elements, and this is clearly shown by the fact that we meet with essentially complicated valency relations when we pass to elements with electro-chemically more decided characters. This is shown by nitrogen, which is trivalent towards chlorine and pentavalent towards oxygen, while different views are held concerning its valency in the ammonium compounds. And the nearer we approach towards the first and last members of the periods of the natural system, the more intricate are the valency relations, which finally become almost chaotic. The facts now show that in the formation of compounds of allied elements small amounts of affinity are saturated, but for the formation of compounds of chemically very different elements, on the contrary, large amounts are used up. As now the amount of affinity contained by the atoms of the elements is always the same, it is to be expected that in the formation of the former high, and in the formation of the latter, on the contrary, lower valency values will be revealed. This is also the case; for in the compounds of the metals with one another (alloys, amalgams, &c.), and in the compounds of metalloids with metalloids (oxides, &c.), actually high valency numbers appear, and in the compounds of the metals with the metalloids, on the contrary, lower values. Unfortunately, I cannot here discuss these relations more fully, and must also refrain from entering on other questions of the valency theory, *e.g.*, the maximum valency number, the change of valency, &c. The developments here described only serve to lay the foundation of the view that a fuller investigation of the valency phenomena of the elements must be based on a general doctrine of affinity.

THE VAGARIES OF BERYLLIUM.*

By CHARLES L. PARSONS.

As it has become a custom in the American Chemical Society for the Chairmen of the various Sections, into which the Sessions of the General Meetings are divided, to present an Address upon some branch of their work in which they are especially interested, I have decided to speak this morning upon beryllium, and especially upon those peculiarities of the element which stand out prominently as characteristic of itself. I realise fully the narrowness of the subject, and fear that what I have to say will scarcely be of interest to all of you, but must plead as my excuse that, realising fully the limitations of my own knowledge, I can select no other subject with which I am more familiar.

Even at its christening beryllium started on a vagarious career, and its early sponsors, as well as those who followed, have recognised it under different names, and have ascribed to it and to its compounds properties as widely variant as the conditions under which they worked. Referred to first by Vauquelin, its discoverer, as "la terre du Béril," the German translators naturally adopted Berylerde as the name of its oxide, and although Vauquelin later accepted, under virtual protest, the suggestion made that glucine be used on account of the sweetish taste of the salts of the element, the name never secured adoption outside of France, and in the early literature was frequently written glycine. When later the element itself was separated by Wöhler he used the term beryllium for the first time, and a few weeks later glucinium appeared in the French press due to Bussy's almost simultaneous discovery. It is useless to go into the subsequent usage of the term, or why the "i" was dropped and glucinum used

* Address by the Chairman of the Section of Inorganic Chemistry at the Toronto Meeting of the American Chemical Society, June 28, 1907.

for a time in American practice. It is sufficient, I think, to say that by far the majority of chemists of the world prefer and use the name beryllium in their conversation and writings, and since neither priority nor usage can be shown for glucinium it should be dropped as rapidly as possible in the interests of uniformity. I especially believe this to be true, since there is no prospect of its ever replacing the more popular and, in my opinion, more justifiable beryllium.

Although the literature of inorganic chemistry is quite generally overburdened with compounds which have no actual existence, and which have obtained place and been assigned formulæ simply by the *analysis* of solid phases obtained under variable conditions, and without other attempt to prove their individuality, it is doubtful if there is any branch of the field that needs more careful revision than the chemistry of beryllium. Its literature is full of errors. Compound after compound has been claimed which has no actual individual existence, but whose place in literature and whose formula depends solely upon analysis of mixed crystals, residues of evaporation, or indefinite gummy precipitates without attempt to separate the individuals present. Formerly this could not always be done, but with the more recent and simple applications of the phase rule to these problems there is no excuse for similar errors which, unfortunately, still continue to creep into our journals.

The metal beryllium itself has been but little studied, and for the main part simply as a dark steel-grey powder obtained by the reduction of its chloride by sodium or potassium, or as small hexagonal plates obtained by the electrolysis of its double fluorides in a manner quite similar to the production of aluminium. Its melting-point, its solution tension, and many others of its important properties have never been determined, and many diverse statements are to be found in regard to it although the very careful researches of Lebeau can undoubtedly be fully relied upon so far as he went into the subject. It is recorded, for example, that it does and it does not combine directly with hydrogen, sulphur, selenium, and phosphorus; that it is and it is not reduced from its oxide by aluminium and magnesium; that it has been produced (even manufactured) by the electrolysis of its bromide, and that its bromide is not a conductor of electricity. In each case the negative is probably true. For many years its valency was, and for that matter still is, a matter of dispute. Even before it was seen that the only vacant place for beryllium in the periodic system was between lithium and boron there were strong arguments for both its divalency and its trivalency on account of its close resemblance to both zinc and aluminium in its action. When Mendeleeff finally pointed out its proper place in his table the controversy grew even more animated, and most of the researches on the element in the seventies and eighties had the establishment of the true valency as the main object. All the early determinations of the specific heat lead to the figure 13·6 as the atomic weight, and it was not until Nilson and Pettersson, after conquering unusual difficulties in a masterly research, finally determined the vapour density of the chloride and established its formula as $BeCl_2$ that real light was thrown on the question. Shortly afterwards, in 1886, Humpidge showed that beryllium was abnormal as to its specific heat, which increased regularly with the temperature at which determined, until between 400° and 500° it approached normal with a value of 6·2. A determination of the vapour density of the bromide, of the acetylacetonate, and of the basic acetate, all seemingly in agreement with the idea of the divalency of the element, would have seemed to have settled the matter, and probably has done so, but the controversy itself goes merrily on. Wyrouboff still argues in his articles for the trivalency, and Tanatar claims that the basic acetate can only be explained on the supposition that the element is in reality tetravalent.

Of the binary compounds of beryllium only the oxide, the carbides, and the halides have any real standing in literature, although the sulphide has been made by Lebeau. Of these the oxide is the only one that is stable in ordinary moist air, and even it shows decided variability in its hydroscopicity for reasons not yet determined. Ordinarily white, it is said to be blue by Levi-Malvano when made from his hexahydrated sulphate, although it is almost inconceivable that the difference of two molecules of water in the sulphate should cause this change. The halides, with the possible exception of the fluoride, can only exist in the complete absence of water, which cause them immediately and violently to lose part of their anion as hydracid. In this respect they are even more sensitive than the corresponding compounds of aluminium. On evaporating their solutions in water they lose more or less of the remainder of the gaseous hydracids, the residue becoming more and more basic, and remaining soluble until a surprising degree of basicity is reached. This hydrolytic action is comparatively small in the case of the fluoride, but is practically complete in the case of the chloride, bromide, and iodide. By careful manipulation residues of almost any degree of basicity, up to the pure oxide, can be obtained, and these mixtures of base and normal salt have given rise to claims for numerous *oxyfluorides* and oxychlorides for the existence of which there is no other evidence than the analysis of the variable residues obtained.

The hydroxide of beryllium is one of the most interesting of its compounds, and one that has properties which vary greatly with the conditions of its preparation. Among the most noteworthy may well be mentioned its great solubility, of from two to five equivalents, in concentrated solutions of its own salts, and its precipitation therefrom on dilution; its solubility in saturated solutions of acid sodium and ammonium carbonates, and its very much diminished susceptibility to reagents when dried at high temperature or boiled in water, as instanced by the fact that when freshly precipitated and washed with cold water, it will take up one-third of an equivalent of carbon dioxide, but on boiling becomes so immune to its action that the gas has been passed through it for three months without any considerable absorption.

Probably the fact which has the greatest bearing upon the chemistry of beryllium, and has caused more failures of researches undertaken upon the element than any other one thing, is the great influence which water has upon all of its salts, acting to many of them almost as if it were itself a strong hydroxide and in a manner that is hard to understand from our ordinary conceptions of solution and hydrolysis.

For this reason normal salts of the non-volatile acids only can be crystallised from water, and, indeed, but very few of them, such as the sulphate, the selenate, and the oxalate, have been so prepared. These are so strongly acid in reaction that they act almost as solutions of the acids themselves, attacking metals with evolution of hydrogen, setting free carbon dioxide from carbonates, and reddening litmus, even after surprising quantities of free base have been added. In spite of this fact the sulphate, chloride, and nitrate have been shown to be less hydrolysed, as determined by the sugar inversion method, than the corresponding salts of aluminium and iron, although they attack metals and carbonates vigorously even after many times enough excess of their own hydroxide has been dissolved to throw back the hydrolysis. Other normal salts like the nitrate can be prepared only by crystallising from concentrated acid, and even anhydrous acid yields only basic compounds in the case of the fatty acid series. Normal salts of more readily volatile acids, like the nitrite and carbonate, have not been produced at all, or only, as in the case of the sulphite, from absolute alcohol, or, as with the halides, by the direct combination of the elements themselves with special precautions to eliminate water. Many normal salts, such as the borates, the chlorates, the bromates, the iodates, the chromates, the acetates, &c., have not beeen obtained apparently because a concentration of acid sufficient to overcome the so-called hydrolytic solution tension of the salts cannot be attained.

On the other hand, only one *acid* salt, the mono-acid phosphate, has any real claim for recognition, and, although the peculiar nature of phosphoric acid would seem to render the existence of this compound as probable as any of an acid nature, its existence rests solely upon the testimony of a single analysis of a non-crystalline precipitate obtained by Scheffer nearly fifty years ago.

The action of water upon the compounds of beryllium is highly modified, as is the case with some of the compounds of aluminium and magnesium, by the entrance of another metallic element into the molecule, and some of the double salts of this element are well defined and readily obtained in the presence of water, where the simple normal salt could not be produced at all or only with difficulty. This is notably true of the double carbonates, chlorides, iodides, nitrites, and sulphites, although in general these salts have been studied but little, their discoverers being content with their identification and analysis. Among the double salts time permits of the mention only of the truly interesting double alkali tartrates and malates studied by Rosenheim and Itsig, and of the remarkable fact that the introduction of beryllium into their molecule enormously increases the molecular rotation of the compound, so that the diberyllium alkali tartrates have from five to six times the molecular rotation of the corresponding alkali bitartrates and the diberyllium malates a molecular rotation more than twenty times as great as the alkali bimalates. This is particularly surprising, since Walden has shown that beryllium has no undue influence upon the molecular rotation of the alpha brom-camphor sulphonates.

Some of the most interesting problems of the chemistry of beryllium lie in the equilibrium relations that exist between the various acid radicals and quantities of the oxide in excess of that required to produce the normal salt, *i.e.*, in the so-called basic compounds. It is certainly true that many of these acids can hold in solution phenomenally large amounts of beryllium oxide or hydroxide, extending in the case of the acetate to six equivalents, while the chloride can hold four, the sulphate three, and the oxalate nearly three equivalents. Even after these abnormal amounts have been dissolved the solutions still remain acid to litmus, and if heated in contact with basic beryllium carbonate the carbonate is attacked, the carbon dioxide set free, and an equivalent amount of hydroxide thrown out of solution. These highly concentrated solutions on being diluted with water throw down precipitates of a highly basic nature, or on evaporation leave gummy masses, the basicity of which depends upon the amount of the dissolved hydroxide, while physically they differ but little. Both the precipitated bodies and the residues of evaporation are amorphous and glassy in structure and vary widely in composition. The basic precipitates on equilibrium being reached approach closely to the hydroxide in composition, but always contain a small amount of occluded acid or normal salt which is impossible to entirely remove by washing. These facts have given rise in literature to a large number of so-called basic compounds which have no existence as independent individuals, but are in reality the impure hydroxide, or perhaps more properly come under the domain of homogeneous phases of variable composition or solid solutions.

It is, indeed, difficult to understand how the solution of the normal sulphate, nitrate, and chloride can dissolve several equivalents of their own hydroxide, attack metals and carbonates almost as vigorously as if they were the free acids themselves yielding these basic solutions, and still be less hydrolysed than the corresponding salts of aluminium and iron, as Leys and Brunner have both shown to be the case. It is, perhaps, equally difficult to demonstrate why the basic solutions so obtained should have less osmotic activity per equivalent of the acid present than the normal salts, should show no indication of a colloidal nature, and should contain no complex anion, but this is, indeed, the fact. The most probable explanation would seem to be that we have here a case of simple solution of a substance (beryllium hydroxide) in a mixed solvent (water and normal salt) in one of which alone (water) it is insoluble. The whole action of these solutions is perfectly analogous to those cases where a substance being dissolved in a mixed solvent *raises* the freezing-point whenever it is insoluble in that component which separates as the solid phase on cooling, and which Lach Miller has mathematically shown is a necessary sequence of the theorem of Gibbs.

In contradistinction to the basic solutions, solid or liquid, already mentioned, we have the truly phenomenal and actually basic compounds of beryllium, discovered in Urbain's laboratory by Lacombe, which are produced pure only in contact with anhydrous acid, or acid so nearly anhydrous that the mass of the water present becomes negligible to produce hydrolysis. These very interesting volatile and perfectly unique basic compounds are apparently confined to the fatty acid series, and have the general formula $Be_4O(AC)_6$. Of these the formate, acetate, propionate, butyrate, isobutyrate, and isovalerianate have been made and studied.

And now after this brief summary of the main characteristics of the chief classes of beryllium compounds I must, in closing, honour those who have been most prominent in developing our knowledge of this element by mentioning the names of Vauquelin, Wöhler, Bussy, Andejew, Weeren, Debray, Joy, Gibbs, Atterberg, Nilson and Pettersson, Humpidge, Hartley, Krüss and Moraht, Lebeau, Rosenheim and Itsig, and Urbain and Lacombe, and paying my sincere respect to the many others who, from time to time, have struggled through the difficulties incident to the peculiar and decidedly vagarious action of this element to greater light and truth. And, finally, I feel that I should call the attention of this Inorganic Section most particularly to the fact that not only the future chemistry of beryllium, but of all the elements in our branch of the greatest of sciences, is becoming more and more dependent for its exactness and wealth of discovery upon the application of those laws which are now correlated under the head of physical chemistry. At the same time we must not be engulfed by this more recent branch of our science, but must always look to her as the handmaiden and not the mistress.

A REVISION OF THE ATOMIC WEIGHT OF POTASSIUM.*

The Analysis of Potassic Chloride.

By THEODORE WM. RICHARDS and ARTHUR STAEHLER.

Introduction.

The atomic weight of potassium is a chemical constant of unusual interest and significance. Standing as it does in the middle of the series of five atomic weights of the most electro-positive metals—substances which exhibit in a highly marked degree both similarity and progressive change in properties—this number must be of unusual importance in the search for that undiscovered mathematical relationship which undoubtedly exists between these constants. Moreover, the atomic weight of potassium is essentially bound up with the atomic weights of oxygen, chlorine, and silver, this group forming a fundamental basis in the calculation of nearly all the other atomic weights; so that a change in the atomic weight of potassium has a widely ramified effect on the whole table of atomic weights. If any further evidence of this fact were needed, the recent paper of R. W. Gray would furnish it (*Journ. Chem. Soc. Trans.*, 1906, lxxxix., 1175).

The recent investigation upon the atomic weight of sodium by one of us in conjunction with Dr. R. C. Wells (Richards and Wells, Carnegie Inst. of Washington *Publication* 28; *Journ. Am. Chem. Soc.*, 1905, xxvii., 459; *Zeit. Anorg. Chem.*, 1905, xlvii., 56) showed conclusively that Stas's work, upon which rested earlier knowledge,

* *Publication* No. 69, Carnegie Institution of Washington.

was somewhat at fault in several respects. The most serious of these errors were, first, the existence of impurity in Stas's silver; secondly, the fact that in his work solid salt was dropped into the argentic solution, causing occlusion of salt; and thirdly, inadequate knowledge concerning solutions of argentic chloride. In view of these errors it seemed not impossible that a similar revision of potassium might likewise yield slightly lower results for potassium than had been found by this master of exact analysis. For this reason the present investigation was undertaken.

Before describing the present work a brief historical review of previous investigations may not be out of place. The determinations may be divided into two groups—the first group including all of these determinations in which the molecular weight of a potassic halide was found by decomposition of a chlorate, bromate, or iodate, and the second group, those in which data for determination of the relation of potassium to chlorine, bromine, or iodine were obtained. The second group alone is concerned with the present work.

The early work of Berzelius, Pelouze, and Marignac need scarcely be considered here. (For a brief discussion of this work Clark's "Re-calculation of the Atomic Weights," 1897, p. 41, may be consulted). It dealt for the most part with the precipitation of argentic chloride from a solution of potassic chloride, and gave very widely discrepant results. Even the later work of Marignac on chloride, bromide, and iodide of silver was of doubtful value, especially the last; and accordingly until the present research was undertaken, the atomic weight of potassium rested chiefly on the analyses of potassic chloride made by Stas, by Richards and Archibald, and by Archibald alone, and upon the analysis of potassic bromide made by Stas.

As in the case of sodium, Stas made several series of determinations of the amount of silver needed to precipitate a known amount of potassic chloride (*Mém. Acad. Roy. Belg.*, 1880, xliii.; also "Œuvres Posthumes," edited by W. Spring; see Clarke's "Re-calculation," 1897, p. 42). One of these series was made in 1865, a later one in 1881, and yet another shortly before his death. The earlier series, although in some respects more careful and thorough than the later ones, was greatly at fault, because in it he overlooked the solubility of argentic chloride. Accordingly, of this work only the later need be considered. The mean of seventeen analyses indicated that 100 parts of silver were equivalent to 69·122 parts of potassic chloride, corresponding to an atomic weight for potassium of 39·130, if silver is taken as 107·93 and chlorine as 35·473. Later, Richards and Archibald (*Proc. Am. Acad.*, 1903, xxxviii., 443; *Zeit. Anorg. Chem.*, 1903, xxxiv., 353) found as a side issue of a research upon the atomic weight of cæsium that 100 parts of silver correspond to 69·115 parts of potassic chloride, and also that 100 parts of argentic chloride correspond to 52·002 parts of potassic chloride; and still more recently Archibald found results not very different (*Trans. Roy. Soc. Canada*, 1904, [2], x., III., 47). With the values given above for silver and chlorine these results indicate a value for potassium of 39·123 and 39·128 respectively, in the case of Richards and Archibald, and 39·122 and 39·135 respectively in Archibald's research.

In the case of the bromide Stas found in an unusually varying series of experiments that 100 parts of silver needed 110·346 parts of potassic bromide for complete precipitation, a result not very far from that of the less precise early work of Marignac. If Baxter's value for bromine (79·953) is accepted (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1322), this corresponds to an atomic weight for potassium of 39·143, noticeably higher than the results from the chloride. At that time the discrepancy did not appear, because the atomic weight of chlorine was not properly evaluated, Stas believing that his work on the chloride also indicated an atomic weight above 39·14.

In view of the fact that these results differ among one another to an extent beyond a reasonable limit of experimental error, it seemed advisable to investigate once more the atomic weight of potassium in order to detect the cause of the discrepancy. This appeared to be especially desirable on account of the recent gain in knowledge concerning the peculiarities of argentic chloride in solution. Accordingly, the present research was begun, and simultaneously another concerning potassic bromide. A description of the latter investigation follows immediately after this one.

An investigation upon atomic weights naturally resolves itself into several different portions—first, the preparation of the pure material; second, the method of drying and weighing this material; third, the details of the analysis and the calculation of the results. These will be considered in order in the following pages. (A somewhat less detailed statement of this work has appeared in the *Berichte*, 1906, xxxix., 3611).

Preparation of the Material.

Potassic Chloride. — Several methods of preparing potassic chloride were tried, the most efficacious being adopted. The problem, of course, was to effect the elimination of other metals and other acids, especially those of the same groups. Both ends are most quickly and completely attained by incorporating into the process of preparation successive crystallisation of different salts, in order to eliminate by the crystallisation of one salt an isomorphous substance which might have been retained during the crystallisation of another salt. The commonest salts of potassium were therefore studied in relation to their fitness for the elimination of impurities in this way.

In the first place, on account of the good results which Richards and Wells have attained in preparing pure sodic chloride from re-crystallised sodic sulphate by precipitation with gaseous hydrochloric acid, sulphate of potassium also was early considered. This method was, however, soon abandoned, because the relative solubilities of potassic sulphate and chloride are far less favourable for the purpose than those of the sodium salts. The method of Archibald, who converted sulphate into chloride through precipitation with baric chloride, is complicated and involves the double work of preparing pure baric chloride as well as pure potassic sulphate. Moreover, it is not easy to eliminate the last trace of baric sulphate from the resulting salt. This also was rejected.

Next potassic chlorate was studied—a salt which had already been used by Stas for the preparation of pure potassium material. Both in crystalline form and in solubility this salt is very suitable for the separation of sodium from potassium material. Sodic chlorate crystallises in regular crystals which are six times as soluble in hot water and sixteen times as soluble in cold water as the monaclinic crystals of potassic chlorate. On the other hand, the data concerning the crystalline form and solubility of the chlorates of rubidium and cæsium are not sufficient to enable one to make any certain prediction with regard to their behaviour, and therefore experiments were made in order to discover whether or not these salts could easily be separated from potassic chlorate by re-crystallisation. The four salts of sodium, potassium, rubidium, and cæsium were mixed together and qualitatively separated by fractional crystallisation. The sodium was effectively separated from the crystals; but after three careful crystallisations the cæsium line, although stronger in the mother-liquor than at first, was still not absent from the crystals. Indeed, neither rubidium nor cæsium lines had considerably diminished therein. Accordingly, this method was also abandoned.

Potassic nitrate showed itself to be much more satisfactory in its behaviour. Its usefulness did not seem at first so certain as to be a foregone conclusion, especially as Stas had not succeeded in preparing a particularly pure material from this salt. Probably this failure was due to the circumstance that he carried out the crystallisation in glass vessels, which of course continually introduced sodium and silica. The rather inadequate data concerning the four nitrates may be well put together as follows :—

Solubility in 100 Parts of Water.

	Cold.		Warmer.		
	Temperature.	Parts.	Temperature.	Parts.	Crystalline form.
$CsNO_3$.	3°	12	60°	Very many	Tetragonal
$RbNO_3$	0°	20	10°	43	Needles
KNO_3 . .	14°	25	114°	337	Rhombohedral and rhombic
$NaNO_3$	15°	84	114°	200	Rhombohedral

Because this series of results is not entirely conclusive, although promising, a series of crystallisations was carried out here also. This series showed that an admixture of the three other nitrates with a large excess of potassic nitrate was nearly all eliminated by as few as two crystallisations. The separation of the sodium was especially marked in the spectroscopic tests. This method therefore appeared very well suited for the preparation of pure potassium material, which might easily be converted into chloride after the other metals had been eliminated.

Pure potassic nitrate of commerce, obtained from Germany, was dissolved in a little water, freed from solid substances by filtration, and crystallised twice in Jena glass flasks. The salt was each time freed from the mother-liquor in a porcelain centrifuge (Richards, *Journ. Am. Chem. Soc.*, 1905, xxvii., 105). The resulting material was four times subsequently re-crystallised in platinum vessels, and whirled in a platinum centrifuge. The pure crystals were now divided into two parts; one part was dried in a vacuum desiccator, while the other part was subjected to yet six more crystallisations and whirlings in platinum vessels.

It now became a question how this nitrate could best be converted into chloride. The method recommended by Stas of heating the salt with pure ammonium chloride involves not only the preparation of this latter salt in a pure state, but also great danger of contamination from the vessel, whether of platinum or porcelain. Platinum is especially attacked because of the action of the oxychlorides of nitrogen and of chlorine. The more favourable method appeared to be to convert the nitrate into chloride by repeated evaporation with hydrochloric acid in quartz dishes. This method was found to have two objections. In the first place, dishes large enough for the raw material were not to be had. Moreover, the tendency of the branching crystals to grow over the edge of the dish caused serious loss of material and danger of impurity. Neither could potassic nitrate be heated to a high temperature with ammonic chloride, or in the steam of hydrochloric acid in quartz dishes; for there is always danger that the reaction $4KNO_3 + 2SiO_2 = 2K_2SiO_3 + 4NO_2 + O_2$ would occur (Richards and Archibald, *loc. cit.*).

Because Stas had never been able to obtain a salt free from silica when working in glass vessels, we desired to avoid completely the use of glass. Therefore, only one way remained, namely, to convert the potassic nitrate into chloride by precipitation with hydrochloric acid in a platinum dish. The resulting aqua regia must naturally attack the platinum, but we preferred this impurity to that of silica, and found, moreover, that the amount of platinum dissolved is very small. In the presence of large masses of potassic salts, aqua regia, especially in the cold, dissolves platinum but little. For example, in one experiment in which about half a kilogrm. of potassic nitrate was treated with hydrochloric acid gas, only three-tenths of a grm. of platinum was converted into the form of potassic chlorplatinate. In subsequent crystallisations the amount was very much less, because the great mass of the nitric acid was eliminated by the first crystallisation. After the third re-crystallisation, the diphenylamin reaction failed to reveal the presence of any retained nitrate.

The precipitation was carried out in the following manner:—The often re-crystallised, very pure potassic nitrate was dissolved in the least possible quantity of cold water, contained in a platinium dish, packed in ice. Slowly, in order to prevent warming, hydrochloric acid gas was run into this solution. The gas was supplied by warming a pure concentrated solution, and was passed into the nitrate solution through an inverted platinum funnel. The potassic chloride, which appeared somewhat yellow from its slight platinic impurity, was whirled in the platinum centrifuge and dissolved in purest water. Potassic chlorplatinate is practically insoluble in a concentrated solution of the chloride, as the law of concentration effect and the theory of ionisation predicts; hence the impurity was easily separated upon a small pure filter. The clear colourless solution was again saturated with hydrochloric acid, and the same round of operations repeated. Upon a third repetition of this process, the nitric acid was eliminated, and the salt, as a rule, was wholly colourless in consequence. On no occasion, even with large amounts of materials, did perceptible colour remain after five treatments. No specimen was subjected to less than seven such re-crystallisations, while some were passed yet five times more through the precipitation and centrifugal drying. Assuming that each time about three quarters of the ordinary adhering mother-liquor was removed by the centrifugal separation, these crystals must have been as free from heteromorphous substances as if they had been re-crystallised many thousand times in the ordinary fashion. It will be shown that all the samples gave the same results upon analysis, hence further purification according to this method was needless. The salt was found to be wholly free from sodium by a sensitive spectroscopic test. It was in every case freed from acid by a single re-crystallisation from the purest water and by fusion in the manner to be described later.

Seven different samples were prepared after this fashion from varying raw material. These are given in the list below.

a. The pure potassic material ("C.P." of German preparation) was re-crystallised as nitrate six times, and precipitated as chloride seven times. This salt after the final re-crystallisation from pure water was dried in a platinum dish at 120° in an electric oven. The salt was snow-white, and was as clear as water when fused, as, indeed, were all the other samples.

b. This sample was similar to *a*, but obtained by the evaporation of the final aqueous mother-liquor decanted from *a*. The mother-liquor from *b* was rejected.

c. Five extra precipitations with hydrochloric gas (or twelve in all) yielded this salt, which was prepared for analysis in the same way as *a*.

d. This salt bore the same relation to *c* that *b* bore to *a*, being essentially identical with *c*.

e. For this sample and the next one the nitrate was re-crystallised twelve times, and the chloride precipitated seven times.

f. From the final mother-liquor of *c*, *f* was prepared, as *b* followed after *a*.

z. This sample was exactly like *a*, except that the raw material came from an entirely different source.

Argentic Nitrate.—The nitrate of silver used for precipitating chlorine in the analysis was crystallised three times from pure dilute nitric acid solution, and each time centrifugally freed from mother-liquor. Before each analysis the aqueous solution of the salt was tested in the nephelometer for a possible trace of argentic chloride, and no material was ever used which showed to this exceedingly sensitive test the least trace of impurity (see Richards, *Proc. Am. Acad.*, 1894, xxx., 385; *Zeit. Anorg. Chem.*, 1895, viii., 269). For preservation in a pure state it was kept in a tight desiccator over potash.

Silver.—The metallic silver used in the research was made from argentic nitrate which had been six times re-crystallised. The metal was precipitated as fine powder by ammonic formate (Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 475), melted on pure lime, and further purified by electrolysis (J. L. Hoskyns Abrahall, *Journ. Chem Soc. Trans.*, 1892, 660; also Richards, *Proc. Am. Acad.*, 1893, xxviii., 22). The beautiful crystals thus

prepared were fused in a stream of pure electrolytic hydrogen, and finally in a vacuum of 0·1 mm. The metal was supported on a boat of the purest lime, prepared from calcic carbonate precipitated from the nitrate for this purpose. The boat was provided with several compartments, each of which held enough silver for one analysis, in order to avoid the possible introduction of impurity into the metal by subsequent cutting. It was enclosed in a stout porcelain tube, provided with Hempel water-cooled stoppers, and was heated electrically in a Heraeus tube-furnace (Heraeus, *Zeit. f. Elektrochemie*, 1902, viii., 201). The vacuum was maintained by a motor-driven Geryk oil air-pump. Except for these minor improvements, the preparation was essentially similar to the best methods employed by Richard and Wells in their often-cited work, to which the reader is referred for further details.

Nitric and Hydrochloric Acids.—Very carefully tested preparations of commerce were used as the raw materials in the preparation of these acids. They were re-distilled with platinum condensers until they were fully pure enough for the purposes for which they were needed. The hydrochloric acid had been shown in the research on sodium to be free from bromine or iodine.

Water.—This substance, because it is used in larger quantities than any other, must be especially pure. All the water used, either for preparation or analysis, was twice distilled, once with alkaline permanganate and once alone. For the best work a platinum condenser was used. All that was needed for analysis was tested in the nephelometer immediately before use.

(To be continued).

CORRESPONDENCE.

RELATION BETWEEN VALENCY AND ENERGY.

To the Editor of the Chemical News.

Sir,—In reply to Mr. le Bas's letter on the above subject (Chemical News, xcvi., 58), I would beg you to insert the following :—

Mr. le Bas states that I assume that the C.H and C.C links have different values; he regards them as having equal values, namely, zero ; which seems to be tantamount to denying their existence.

A priori we must regard every link as being equivalent to so much energy, and naturally until proof is offered to the contrary we must regard different links as corresponding to different amounts of energy; thus my treatment of the question involves no assumption.

If we may assume that the C.C and C.H links have equal values, then we may with equal truth assume any and all links as equal, from which it would follow that most chemical changes would be unaccompanied by heat changes, which is contrary to fact. This shows the assumption to be untenable.

Mr. le Bas's letter contains the extraordinary statements that the heat of combustion of an isolated carbon atom is represented by $C+4\frac{L_1}{2}$, and that of an isolated hydrogen atom by $H+\frac{L_1}{2}$. It is apparent that he is using my constants with a different meaning from that which I applied to them.

I would beg to suggest a perusal of the opening paragraphs of my article in the Chemical News (xcv., 301), also the definitions given in the former article (Chemical News, xcv., 193).

The heat of combustion of an isolated carbon atom is the algebraic sum of the heats due to the severance of one O=O link, and the formation of one molecule CO_2 from its constituent atoms, dealing with a grm. atomic weight of carbon ; it is by definition equal to C cals.

The heat represented by the expression $C+4\frac{L_1}{2}$ cals. is, however, the algebraic sum of the above and the heat due to the severance of 2 C.C links ; Mr. le Bas therefore assumes that no heat is either absorbed or evolved when this link is severed, *i.e.*, $L_1=0$; which apparently he is attempting to prove. Similarly for hydrogen.

The use of the symbols :C: and H. for isolated carbon and hydrogen atoms respectively in this connection, is misleading, for I have already employed them to stand for combined atoms (*i.e.*, :C: stands for a carbon atom plus four links of some sort, and H. for a hydrogen atom plus one link), as was apparent from the context. Thus, I stated that :C: had different values in CH_4, C_2H_6, &c., not because the value of the carbon atom itself was altered, but because it was linked differently.

Examining Mr. le Bas's "proof" that $L_1=L=0$, we find him arguing in a circle ; I have pointed out one occasion on which he assumes this equation ; moreover, the assumption $L_1=0$ is made in calculating the values of C and H, for he states :—

$$2H = \text{M.H.C. } CH_4 - [CH_2] = 210{\cdot}8 - 158{\cdot}2 = 52{\cdot}6 ;$$

whereas, making no assumption, it should be (using Mr. le Bas's figures) :—

$$2H - L_1 = C + 4H - [C + 2H + L_1] = 210{\cdot}8 - 158{\cdot}2 - 52{\cdot}6,$$

whence $H - \frac{L_1}{2} = 26{\cdot}3$.

Thus, all that is proved that $H - \frac{L_1}{2} = H - \frac{L_1}{2}$, which was self-evident before ! (see Note).

(Note.—I consistently use the symbol H to stand for the value of one hydrogen atom plus the value of one C—H link).

With regard to Mr. le Bas's hypothesis, he admits that it is inadmissable to apply the relation $c = \frac{\text{M.H.C.}}{W}$ to unsaturated compounds, *i.e.*, he admits that M.H.C. is not equal to W.*c*. in these cases ; this is what I wanted my figures to point out.

Mr. le Bas now proposes the following formulæ :—

For olefins, M.H.C. $C_nH_{2n}|=|=6n\,c+|=|$; and for acetylenes, M.H.C. $C_nH_{2n-2}|\equiv|=6n\,c-2c+|\equiv|$, where $|=|$ and $|\equiv|$ are constants ; but these equations are in direct contradiction to the statement made by Mr. le Bas (*Proc. Chem. Soc.*, xxiii., 134), that the molecular heats of combustion of the hydrocarbons are proportional to their valency numbers W, and I take it to be a tacit admission that this statement is incorrect.

The question of trimethylene I have dealt with at some length (Chemical News, xcv., 302).

The value $c=26{\cdot}25$ is calculated thus :—According to Mr. le Bas's hypothesis c is the heat equivalent of one hydrogen atom expressed in large calories ; moreover, according to him the value of the C.H and C.C links are negligibly small so that—

$$c = \tfrac{1}{4}(2H - L_1) = \tfrac{1}{4}\beta = 26{\cdot}25.$$

The correctness of my values for the "fundamental constants" (α, β, γ, δ) is proved by the *very small* differences between the experimental and my calculated results.

Mr. le Bas stated in his note in the *Proc. Chem. Soc.* that the heat of combustion of a substance may be regarded as made up of (*a*) an absorption of heat due to the dissociation or decomposition, and (*b*) an evolution of heat due to the combination of the isolated atoms with oxygen ; he further stated that the factor (*a*) is negligibly small compared with (*b*). This latter statement is an assumption, and I have pointed out that it is incorrect because two at least (though not necessarily the C=C and C≡C, and possibly all three) of the various carbon links have large values, as is apparent from the values of the expressions L_2-2L_1 and L_3-3L_1.

Mr. le Bas does not refer to my criticism regarding the use of uncorrected M.H.C.'s,

It is not suggested that Mr. le Bas's hypothesis (rightly stated) is valueless, for the general equation, of which only particular cases have been noted, can be deduced by means of my own constants, the validity of which I have demonstrated; thus, in the general expression for a hydrocarbon put $L_2 = 2L_1 + T_2$, $L_3 = 3L_1 + T_3$, and also add T for any other tension (see Chemical News, xcv., 301); then we obtain—

$$nC + 2(n+1-a-2b-f)H + (n+f+a+2b-1)L_1 + aT_2 + bT_3 + T = na - (n+f+a+2b-1)\beta + aT_2 + bT_3 + T,$$

but *approximately* $4\beta = a$; therefore the above expression—

$$= (3n+1-a-2b-f)\beta + aT_2 + bT_3 + T$$
$$= \{\tfrac{1}{4}n + 2(n+1-a-2b-f)\}k + aT_2 + bT_3 + T, \text{ if } k = \tfrac{1}{4}\beta.$$
$$= W.k + aT_2 + bT_3 + T, \text{ which is the general expression.}$$

It must be, however, carefully noticed that this should be only regarded as a "working rule," and not as a law from which we should be likely to obtain any knowledge of valency, for the following reasons:—1. It depends entirely on the accidental relation $4\beta = a$, and thus does not hold for compounds other than hydrocarbons in general. 2. It is approximate only—not accurate—as I have shown; the error introduced by saying $4\beta = a$ becoming noticeably large for hydrocarbons of high molecular weight. It should also be noticed that k is not defined as the thermal equivalent of an isolated hydrogen atom.—I am, &c.,

H. Stanley Redgrove.

The Polytechnic, Regent Street, W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

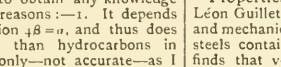
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 5, July 29, 1907.

Ortho- and Pyroarsenic Acids.—E. Baud.—The hydrate, $As_2O_3.4H_2O$, is deposited in a crystalline state in the cold from a concentrated solution of arsenic acid, and when it is heated to 110° $2As_2O_3.3H_2O$ is obtained. The former, when kept over sulphuric acid for several days under a clock-glass, remains unaltered provided that the temperature does not exceed 10°, but above this temperature, *i.e.*, at about 15° or 20°, the crystals effloresce, and lose exactly $2H_2O$. The product is $As_2O_3.2H_2O$, or pyroarsenic acid. Orthoarsenic acid can exist only in solution. When its solution crystallises it leaves the hydrate of pyroarsenic acid, which effloresces at about 15°, and gives pyroarsenic acid. From the thermic point of view the latter is closely analogous to pyrophosphoric acid.

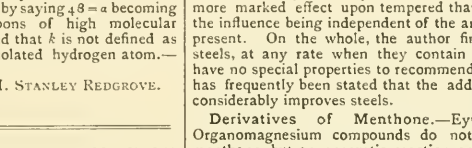
Direct Oxidation of Phosphorus.—E. Jungfleisch.—The products of the direct and spontaneous oxidation of phosphorus at a low pressure are not the same as those formed when the pressure is high. In pure oxygen at atmospheric pressure the oxidation of pure dry phosphorus in the cold gives exclusively phosphoric anhydride; in the same gas at a pressure of 18 to 20 mm. the products of oxidation are phosphorous anhydride, P_2O_3, and a bright yellow compound, which, when dissolved in alcoholic potash and precipitated by hydrochloric acid, gives the suboxide, P_4O. The process of oxidation is accompanied by characteristic phenomena, the P_2O_3 bursting into flame spontaneously. Whenever oxygen acts at a low pressure upon phosphorus, whether the pure gas, air, or a mixture of oxygen and an inert gas is used, the results obtained are always the same. In presence of water the substances produced by its action on the same compounds are obtained, and this oxidation of phosphorus at low pressures may render it spontaneously inflammable in air in the cold. For instance, if pieces of pure dry phosphorus are placed in a tube closed at both ends by rubber corks, and the tube is filled with carbon dioxide and left in air, after some time the phosphorus near the corks begins to tarnish on the surface, while further from the ends of the tube it remains unchanged. The oxygen of the air diffuses through the corks, and slowly reaches the phosphorus, covering it with P_2O_3 and the yellow compound. Then the pieces of phosphorus near the ends catch fire owing to the spontaneous combustion of the P_2O_3. The phosphorus which has not been reached by the oxygen remains unchanged, and does not catch fire. The same transformation into spontaneously inflammable phosphorus is effected much more rapidly if the apparatus is closed by a thick rubber tube, through the walls of which the diffusion of oxygen takes place more quickly. Phosphorus also becomes spontaneously inflammable when P_2O_3 is formed even in very small quantities on its surface, under various circumstances which the author has investigated.

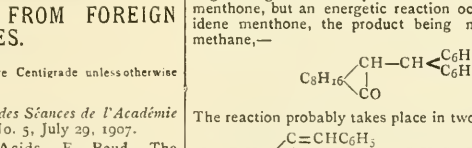
Properties and Constitution of Tantalum Steels.—Léon Guillet.—The author has examined the micrography and mechanical properties of normal and tempered tantalum steels containing different percentages of tantalum, and finds that very small quantities of the element have a more marked effect upon tempered than annealed steels, the influence being independent of the amount of tantalum present. On the whole, the author finds that tantalum steels, at any rate when they contain but little carbon, have no special properties to recommend them, although it has frequently been stated that the addition of tantalum considerably improves steels.

Derivatives of Menthone.—Eyvind Bœdtker.—Organomagnesium compounds do not act upon ethyl menthone, but an energetic reaction occurs with benzylidene menthone, the product being menthoethylphenyl methane,—

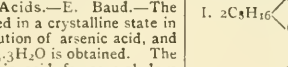


The reaction probably takes place in two stages:—





If ethyl bromide is replaced by phenyl bromide menthodiphenylmethane,—



is obtained. When benzoylchloride is added to the mixture of benzylidene menthone and magnesium phenyl bromide, stereoisomers are produced, two of which the author has isolated by fractional crystallisation in alcohol. The author has also prepared menthomethyl-, normal propyl-, isobutyl-, and isoamyl-phenylmethane, but as yet he has obtained them only in the form of syrups, which are shown by analysis to be impure.

Two New Glucosides, Linarine and Pectolinarine.—T. Klobb.—In the flowers and leaves of *Linaria vulgaris* two glucosides occur; one of these substances, which has been called linaric acid, has been shown by the author, in collaboration with M. Fandre, to be insoluble in ammonia and also in alkaline carbonates, and it is therefore not an acid; they proposed the name linarine for it. When

oxidised it yields a volatile substance, $C_9H_{10}O_2$, and it behaves like a very stable glucoside, which is not hydrolysed by weak acids at the temperature of the water-bath, but is split up by 10 per cent hydrochloric acid at 100—110°, and by concentrated hydrochloric acid in the cold. The second substance, pectolinarine, is also a glucoside, but it easily splits up with weak acids. It differs from linarine by its additional water of constitution. Both glucosides give on hydrolysis a sugar and a mixture of crystalline substances, linaric phenol and anhydrolinaric phenol. By the action of alkalis pectolinarine is transformed into a β-modification, which on hydrolysis gives only linaric phenol, and linarine under the same conditions gives a β-modification, which when hydrolysed gives only anhydrolinaric phenol. Pectolinarine is nearly insoluble in cold water, but dissolves in boiling water and in alcohol, giving solutions which, when saturated, gelatinise on cooling. It is very soluble in concentrated hydrochloric acid and in caustic potash, and when boiled for a long time with water it is transformed into crystalline linarine, losing water of constitution. The formula of linarine appears to be $C_{50}H_{50}O_{25}$, and if the sugar formed is a hexose the hydrolysis can be represented provisionally by the equation—

$$C_{50}H_{50}O_{25} = \underset{\text{Linaric phenol.}}{C_{19}H_{14}O_7} + \underset{\text{Anhydrolinaric phenol.}}{C_{19}H_{12}O_6} + 2(C_6H_{12}O_6).$$

No. 6, August 5, 1907.

Platinum Silicide and a New Double Silicide of Platinum and Copper.—Em. Vigouroux.—Platinum silicide of formula $PtSi$ is formed by the direct union of the elements provided that excess of silicon is present. When this silicide is heated with aluminium it tends to decompose, while copper gives a residue containing traces of silicon and 99 per cent of platinum. The copper silicide, $SiCu_4$, appears to act as a reagent effecting combination, either with this platinum silicide or with free platinum, giving in the latter case a compound of formula $SiCu_2Pt$.

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DIMINUTION IN LENGTH OF COTTON AND LINEN FIBRES DURING THE PREPARATION OF "STUFF" FOR THE MANUFACTURE OF PAPER.

By CLAYTON BEADLE and HENRY P. STEVENS

As very little work has been done in the direction of measuring the actual length of the fibres during the process of beating in the preparation of pulp for the manufacture of paper, the authors made arrangements with a well-known firm of paper-makers to withdraw samples of pulp from the hollanders, of the ordinary type and of about 3-cwt. capacity, during the beating operation, and whilst the beaterman manipulated the roll in the ordinary way for the manufacture of the paper that he had to provide for. In this manner, in the work about to be described, samples of pulp were taken every hour. There was no attempt to determine the length of the fibre at the commencement of the beating, as when the fibres are in the condition of rag "half-stuff" it is almost impossible to arrive at even an approximate estimate by means of measurements under the microscope. It might be assumed, however, that the cotton and linen fibres as "half-stuff" are intact, and therefore an average length of each, based on published figures, may be taken as representing the length of the fibres as half-stuff. As, however, such a figure is a pure assumption, the length of fibre is given in tables and curves as from the end of the first hour in each case. Furthermore, measurements made at an earlier stage in the beating would have no practical value.

With very long stuff, or stuff that has been very little beaten, it is extremely difficult to arrive at the average length, because it requires a great deal of experience to obtain on the "field" a representative set of fibres, many of them being in the form of threads or small woven particles. When, however, the work of unravelling the threads is accomplished the measurement can be more easily made. Where possible, two sets of readings were taken of each sample, each set consisting of ten determinations for length and diameter. The measurements were made under a magnification of seventy-two diameters. The average of each set should bear a fairly close correspondence with one another, and each set should be the result of measurements of different "fields." As indicating the extent to which the individual fibres varied in length, we give in Table I. details of measurements for the ninth hour. In Table II. we give a summary of this trial on linens beaten for ten hours. Tables III. and IV. are summaries of similar trials.

It will be noticed that, in the case of Table II., there is, with one or two exceptions, a decrease in length of the fibre from hour to hour. The same will be noticed in respect to Tables III. and IV. Where the fibres showed any marked irregularities, the work was carefully repeated, and it was finally found that, in the case of the linens, a diminution in length could be represented by Curves A and B.

In the case of the cottons (Curve C) the diminution is apparently somewhat spasmodic, the result possibly of a

Table I.—*Details of Measurements of Linens after Nine Hours' Beating.*

Length. Mm.	Length. Mm.
2·92	1·87
2·64	3·82
2·43	2·22
2·50	1·74
2·16	2·92
2·71	2·82
2·85	2·78
1·81	2·78
3·61	3·61
3·82	3·40
Mean .. 2·74	2·80

Mean length of twenty readings .. .. 2·77 mm.
Mean diameter of first ten readings .. = 0·0187
" " second ten readings = 0·0181
" " twenty readings .. = 0·0184

Table II.—*Examination of Linen Pulp at different stages of the Beating for Length of Fibre.* (See Curve A).

(Beaten for 30 lbs. 21" × 33").

Hours of beating.	Average length. Mm.	Average diameter. Mm.
1	13·3	0·0222
2	9·4	0·0227
3	5·62	0·0260
4	4·37	0·025
5	3·92	0·023
6	3·37	0·021
7	3·58	0·020
8	2·89	0·0185
9	2·77	0·0184
(*a*) 10	2·14	0·023

(*a*) Taken on fibres from finished paper.

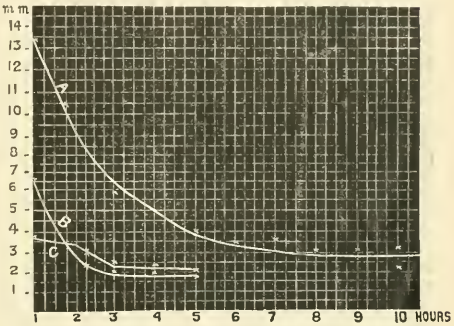
Table III.—*Linens Beaten for Five Hours at different stages of the Beating.* (See Curve B).

Hours of beating.	Average length. Mm.	Average diameter. Mm.
1	6·34	0·0177
2	2·84	0·0190
3	1·82	0·0186
4	1·94	0·0174
5	1·70	0·0199

Table IV.—*Cotton ("Scotch Fines") at different stages of the Beating.* (See Curve C).

(Beaten for 100 lbs. Imperial).

Hours of beating.	Average length. Mm.	Average diameter. Mm.
1	3·59	0·0185
2	3·40	0·0180
3	2·34	0·0208
4	2·26	0·0184
5	2·02	0·0181



Curves showing the Diminution in Length of Cotton and Linen Fibres during the Process of Beating from Rags.

sudden lowering of the beating roll. It will be noticed that, in the Curves A and B, during the first two hours there is a very great diminution in length, but during the second half of the beating the length is only influenced to a comparativly small extent. No doubt had we been able to take the actual length of the fibres before the beating commenced, we should have found possibly as much diminution during the first hour's beating as was to be noted in the other nine hours. Such curves have, as far as we are aware, never before been constructed.

The authors wish to express their thanks to their pupil, Mr. G. W. Ross, for his assistance in connection with the measurements.

THE ORIGIN AND OCCURRENCES OF THE DIAMOND.*

By Professor T. W. E. DAVID, F.R.S.

DURING the session of the British Association for the Advancement of Science at York in 1906, an interesting discussion was started on the above subject in connection with the exhibition of a diamond in the original matrix by Professor David. This specimen was discovered by Mr. A. R. Pike, of Oakley Creek, Copeton, near Inverell. Mr. E. F. Pittman, Assoc.R.S.M., Under Secretary for Mines and Government Geologist, has already recorded this occurrence and described the locality referred to in the annual report of the Department of Mines, N.S.W., 1904. He has also recorded the occurrence of diamonds in matrix at the Ruby Hill mine, on the road from Bingara to Tamworth. It may be mentioned that at the latter locality the rock considered to be the probable matrix of the diamond is of a mixed character. Portion of the hill is formed of agglomerate or volcanic breccia, covered by loose boulders of basalt. This agglomerate is traversed by dykes of basalt, and contains garnets and inclusions of a rock called eclogite. The eclogite rock is a rather coarsely crystalline mixture of garnet, lime, felspar, and the mineral known as diopside.

The diamonds which have been found in this locality are considered by Mr. Pittman to have been derived either from the volcanic breccia or from the basalt dykes which intersect it. Up to the present no undoubted specimen of this volcanic rock with a diamond actually in matrix in it has yet been found. The discoverers, however, Messrs. Pasley, Gordon, and Morkel, maintain that ten diamonds have been obtained by them at this mine from volcanic breccia taken out of their shaft and washed in a tub with a hand sieve. These ten diamonds are stated by Mr. Pittman to have weighed in the aggregate 4¼ carats. He adds that the diamonds were remarkable in that they each had a distinct depression of pitting on one of the faces. As will be recorded presently, similar phenomena may be noticed in the case of the diamonds more recently discovered in matrix at Oakey Creek. The latter discovery was the result of a theory held by Mr. A. R. Pike (of Messrs. Pike and O'Donnell) that the Copeton diamonds must have originated in certain local dykes or pipes. This view he has entertained for years, and after much patient work his researches were rewarded by the discovery of a diamond actually *in situ* in a lump of basis rock taken out of a tunnel which was driven through a 26 ft. thick pipe of dyke. This beautiful specimen of diamond in matrix shows it to be about two-thirds embedded amongst the crystalline minerals of the igneous rock. At a meeting of the British Association at York, England, as well as at the International Geological Congress of Mexico last September, this specimen was most critically examined by the chief scientific authorities on diamonds in the world, and all were satisfied as to the absolute genuineness of the discovery, and considered it of the highest possible scientific interest.

With a view of throwing light upon the nature of the rock forming the matrix of the diamond, a couple of thin slices were cut off from a corner of the diamond-bearing matrix. These were rubbed down by a lapidary until they were sufficiently thin for their constituent minerals to be recognised. It was then clearly demonstrated when the thin slices of the rock were placed under a microscope that the rock was quite unlike any which has hitherto been proved to form a matrix of the diamond in any other part of the world. This fact of course lends additional interest to Mr. Pike's discovery at Oakey Creek.

In addition to the remarkable specimen above referred to, a second diamond was exhibited by Professor David, both at York and Mexico, coming from the same mine. This diamond is about the same size as the first, and was picked up from off a heap of igneous rock at grass at the mouth of the tunnel at Oakey Creek. It was shed from a disintegrated fragment of the dolerite in the process of its becoming decomposed under the action of the weather. There can be no doubt from the statements of the finders that this diamond was not of alluvial origin, but was actually shed from the matrix itself. Moreover, even apart from the actual record of how it was found, the diamond bears internal evidence of having been derived direct from the original rock matrix. Professor Bonney, at York, called special attention to the interesting fact that the surface of this diamond was deeply pitted, and that portions of the original diabase matrix were embedded in the small pits. A careful microscopic examination of them showed that these little inherent fragments of matrix corresponded exactly in their contained minerals, &c., with the general character of the rock forming the matrix of the specimen first described. Messrs. Pike and O'Donnell treated about two loads of partly decomposed igneous rock from the same tunnel on their mine, and hand-sieved it; and although by far the greater part of the material so treated was thrown back in the form of lumps into the heap from which it was originally taken, two diamonds were obtained from it. The material treated in this primitive way weighed about 2 tons. Although about 45 tons of igneous rock have been mined, this has been stacked; and it is the intention of the syndicate to whom the mine now belongs to put this decomposed material, now in the form of rock lumps, through a rotary puddling plant such as is used in Africa. Water is, of course, needed for the purpose, and the syndicate are waiting until the present work they have in hand will give them the necessary supplies. The delay in further testing this 45 tons of igneous rock for diamonds has been entirely due to want of water. Until such tests are carried out it would be premature to hazard an opinion as to whether or not the mine where this very interesting discovery has been made is likely to prove remunerative.

The exhibition, particularly at York, of the two specimens of diamond above referred to and the discussions which ensued created the greatest possible interest amongst the assembled scientists. In the first place, with regard to the rock which forms the matrix of the diamond at Oakey Creek, this was examined both in the hand specimen as well as in the form of thin microscopic slides. A very complete chemical analysis of the rock was submitted both at York and Mexico. This had been prepared by Mr. Mingaye, analyst and assayer to the Geological Survey Branch of the Department of Mines, Sydney. The result of the microscopic examination, taken in conjunction with the nature of the analysis submitted, led them to class the rock as belonging to the variety known as hornblende-diabase. In no other part of the world has a diamond ever been found in a rock matrix like this. Hitherto the occurrence of diamonds in matrix, until this recent discovery by Mr. A. R. Pike, was restricted to the following kinds of rock:—

1. *The Diamond-bearing Volcanic Pipes of South Africa.*—These have the shape of roughly circular pipes, often

* From the *Mining Journal*, August 24, 1907.

several hundreds of yards in diameter. They appear to have formed the chimneys or explosion hollows connected with some violent deep-seated volcanic action. The rock which now fills them, and which therefore holds the diamonds, is of a fragmentary character of the nature of a breccia or agglomerate. The enclosed fragments are chiefly of igneous origin, and are formed mostly of dark and heavy eruptive rocks, some of which are allied to serpentine. It is interesting to note that in this breccia there are numerous fragments of a garnet-bearing rock, eclogite, very similar, as Mr. Pittman has pointed out, to the rock of the same name discovered at Ruby Hill, in New South Wales.

2. *Occurrence in Gneiss in Brazil.*—The only other occurrence of diamond in matrix in a terrestrial rock is perhaps that of a diamond in a specimen of gneiss found in Brazil.

3. *Meteoric Occurrence.*—The third form of occurrence is extra-terrestrial, and may be described as meteoric. Diamonds have been discovered in the nickel-iron meteorite of Canyon Diablo, in the south-west of the United States, not far from the Grand Canyon. Diamonds have also been discovered in the stony meteorite from Novo Urie, in Russia. It may be mentioned that some very curious hollow cubes of carbon in the form of graphite, discovered in the meteorites at Youndigin, in Western Australia, and provisionally classed as the mineral cliftonite, are now generally looked upon as pseudomorphs, after diamond—that is, cubes of carbon, which, while they retain the original physical constitution of that gem, becoming black and opaque, are very soft; in fact, in general physical character and composition closely resembling the carbon of a black-lead pencil. If this view as to their origin is correct the diamonds of the Youndigin meteorites were of much more than mere microscopic size.

The question may next be considered—Is there any possible light on the genesis of the diamond to be derived from its artificial manufacture? Amongst very numerous experiments on the subject the following three may be specially selected:—

Following up the clue given by the occurrence of microscopic diamonds in the Canyon Diablo meteorite, the distinguished chemist and mineralogist, H. Moissan, of Paris, has succeeded in manufacturing microscopic diamonds artificially by fusing sugar charcoal at a very high temperature in the electric furnace in various metals—iron, silver, lead, &c. In order to make the experiment a success the carbon of the sugar charcoal has to be introduced suddenly into the crucible containing the molten metal, otherwise of course it would be completely burnt away through oxidation. Immediately the metallic casing holding the sugar charcoal has been dissolved in the molten metal the crucible is removed from the furnace, and is plunged into cold water, or preferably into a bath of molten lead. This has the effect of readily cooling the exterior of the small molten mass. The crucible is then removed from the water or lead, and the cooling is allowed to be completed at a slower rate. In the process of this cooling enormous pressure is exerted by the contracting shell of solidified metal on the still molten nucleus inside containing the dissolved carbon. When this nucleus ultimately solidifies the carbon crystallising out under such conditions of intense pressure forms microscopic diamonds, some of them of the nature of black diamond, but others clear and translucent.

"A second method of manufacturing diamonds artificially is that adopted by Dr. Friedlander, of Berlin. This distinguished experimenter was present at the Mexican Congress, and was intensely interested in the Oakey Creek specimens. His method is to take some splinters of the mineral olivine (a silicate of iron and magnesia, very commonly found in blue metal or basalt), and to fuse it up before the oxy-hydrogen blowpipe, stirring the molten mass the while from time to time with graphite, in the form of the carbon of a blackleaf pencil. When the fused mass is cooled down he removes by means of suitable chemical reagents all the non-diamond minerals, and usually finds a small residue of true microscopic diamonds. The scientific world was at first inclined to question the accuracy of Dr. Friedlander's results, but he has since been able to amply demonstrate their correctness, and they are now generally accepted by the scientific world.

The third method of diamond manufacture is that to which Sir William Crookes has recently called attention, and it is of great scientific interest. He held that the diamond was probably formed under conditions where there was no access to free oxygen, for he contended that the presence of oxygen, even under the condition of its occurrence in molten silicates, if at a high temperature, would lead to the oxidation and subsequent destruction of diamonds. He therefore thought it probable, first, in view of Moissan's experiments, secondly from the well-known fact that diamonds have been met with in nickel iron meteorites, that the original matrix of the diamond was metallic iron. He has also drawn special attention to the following interesting fact:—"Carbon and arsenic are the only two elements that have a melting-point above their boiling-point; and among compounds carbonic acid and fluoride of silicium are the only other bodies with similar properties. That is, these solids, when highly heated, pass off direct into vapour without going through an intermediate liquid stage, as water substance, in the form of ice, does when its temperature is raised, as obviously the ice passes into water before the latter can be converted into steam. Now the melting-point of arsenic is about 1·2 times its absolute boiling-point. With carbonic acid and fluoride of silicium the melting-points are about 1·1 times their boiling-points. Applying these ratios to carbon, we find that its melting-point would be about 7460° F. With a temperature of 7460° F., a pressure of about 250 lbs. to the square inch would be the necessary melting-point pressure for carbon, as calculated, by Sir William Crookes. Any pressure, therefore, above 250 lbs. per square inch would suffice to liquefy carbon at the above temperature. In order to verify his theory that diamonds can be formed from carbon melted under the above conditions of temperature and pressure, Sir William Crookes was unable to avail himself of the electric furnace, as its maximum temperature falls distinctly below the amount postulated. As stated, however, by him, Sir Andrew Noble was able, by exploding cordite in a closed steel cylinder, to obtain a pressure of 8000 atmospheres, or 50 tons per square inch, with a temperature reaching in all probability about 9260° F. He adds:—"Here, then, we have conditions favourable for the liquefaction of carbon, and were the time of explosion sufficient to allow the reaction to take place, we should certainly expect to get the liquid carbon to solidify in the crystalline state." On subsequently examining some of the residues obtained from these closed vessels after the explosions, he succeeded in discovering microscopic crystals of true diamond. These were critically examined by Professors Bonny and Miers, who agreed with Professor Crookes that the crystals could be none other than octahedral diamonds showing characteristic cleavage, refractive index, &c. Thus, Sir William Crookes concludes that diamonds were originally formed probably at a very high temperature, and under sufficient pressure to admit of the carbon melting before it boiled, and also under conditions where there was no free access of oxygen, even in the form of silicates.

In the discussion on the genesis of the Oakey Creek diamonds, Sir William Crookes argued that the original matrix of the diamond in this case, as in South Africa, in his opinion, had been metallic iron in the first case. An obvious difficulty is the explanation of how the diamonds have become released from their iron prison. The diamonds may possibly have been set free, either by an oxidation of the iron or by the iron becoming molten while the diamond still remained solid, in which case, on account of the specific gravity of the diamond being much less than that of the iron, the diamond would at once come to the surface of the molten iron, just as a cork after being submerged

and suddenly released comes to the surface of the water. Professor David replied to Sir William Crookes that in Dr. Friedlander's experiments diamonds had actually been manufactured from graphite carbon in a molten silicate, and also that natural diamonds had been discovered in the stony meteorite of Novo Urie in Russia, and that there is therefore clear evidence to show that it is possible for diamonds to form in the presence of silicates, in spite of the fact that the latter contain oxygen.

Both Professors Bonney and Cole argued at York that even in the case of the South African diamond pipes the diamonds are not really *in situ*, but may have been derived from older masses of rock which have become churned up and largely fused in the local diamond pipe of volcanic origin. According to this contention, diamonds, when we find them now in matrix in rocks of the earth's crust, are the sole survivors of a whole group of minerals which in the long process of their transfer from deep-seated portions of the earth's crust to the earth's surface have become attached by the transporting molten rock, and dissolved in it.

According to the views of the above scientists, all diamonds have originally been formed in very old crystalline rocks, and where we now find them in a rock like the hornblende-diabase of Inverell their survival there is due to their superior infusibility, hardness, &c., as compared with these qualities in the constituent minerals of the original rock in which the diamonds grew.

Certainly in many parts of the world diamonds are of very high geological antiquity, a fact which is in favour of the view that they were derived originally from ancient crystalline rocks. For example, in one of the most famous diamond fields of India—that of Panna—the diamonds occur as transparent crystals, derived from the very ancient Vindhyan sandstones and conglomerates. Dr. Vredenburg, of the Geological Survey of India, in his recently published report on this subject, argues a derived origin for all the diamonds, not only of Panna, but as far as he knows of the whole of India. The age of these Vindhyan diamond-bearing sandstones is now, considered by Dr. T. H. Holland to be extremely ancient, referable probably to the Algonkian division of pre-Cambrian time.

In Western Australia diamonds have been discovered in a very ancient conglomerate, probably older palæozoic, worked mostly for the sake of its gold. It was found that at this mine at Nullagine, near Pilbarra, in Western Australia, the steel dies of the stampers and the stamper boxes were being constantly worn away at a comparatively rapid rate. A careful examination revealed the presence of microscopic diamonds derived from these conglomerates, and Mr. Gibb Maitland, F.G.S., the Government Geologist, is satisfied as to the genuineness of the discovery.

In South Africa also Dr. F. Hatch has shown that derived diamonds are met with on the geological horizon of the Witwatersrand conglomerates, the age of which is usually assumed to be at least as old as Devonian.

If it be conceded that all the diamonds of the world were generated in crystalline rocks of high geological antiquity, then it would follow that both in the diamond pipes of South Africa, which are newer in age than the Sydney sandstones, that is post-Triassic, as well as in the hornblende-diabase dykes or pipes of Inverell, which are later in age than our coal measures, that is post-permo-carboniferous in age, the diamonds are transported minerals, and therefore of an earlier origin, than the rocks in which they are now embedded. Of special interest in connection with this theory is the second Oakey Creek diamond exhibited to the Science Congress. This diamond was set free by weathering from the matrix. The diamond shows comparatively deep indentations of its surface, in-filled with portions of the hornblende-diabase matrix. It is not as yet certain whether these indentations are due to the removal by corrosion or resorption of minerals which crystallised out originally with the diamond, at the same time as the diamond came into being, or whether they represent negative crystals etched out of the diamond itself by the substance of the volcanic dyke in the process of the floating up of the diamond in the molten mass of the dyke to the earth's surface from considerable depths beneath. These indications at all events show that the diamonds in the hornblende-diabase of Oakey Creek are of somewhat earlier origin than their surrounding minerals, perhaps in the same sense as are the quartz crystals of rocks like rhyolites and quartz-porphyries. If, therefore, diamonds can be generated at various geological ages, and there seems to be no reasonable physical or chemical grounds for doubting this, Professor David pointed out at the Congress that it would seem just as reasonable to suppose that these Oakey Creek diamonds are really *in situ* in the hornblende-diabase, as to suppose that the quartzes of rhyolites and quartz-porphyries are practically *in situ*, and the latter view is now generally admitted to be practically established.

Much yet remains to be done in the way of further prospecting the scene of this interesting discovery at Oakey Creek, and it is to be hoped that, as the result of further study, fresh light may be thrown on the at present dark problem as to the mode of origin of the diamond, and that the find will ultimately prove to be not merely highly interesting scientifically, but also remunerative.

Already quite a number of scientists at the Congresses at York and Mexico have expressed their desire to work out details as to the mode of origin of these New South Wales diamonds. Among them may be specially mentioned the names of Professor Bonney, Professor Miers, of Oxford, Professor Offret, of Lyons, Dr. Friedlander, of Berlin, and Mr. Kunz, of the great and well-known firm of Tiffany, New York.—*Sydney Morning Herald.*

THE

APPLICATIONS OF GRIGNARD'S REACTION.*

By ALEX. McKENZIE, M.A., D.Sc., Ph.D.

Introductory.

In 1900 Victor Grignard (*Comptes Rendus*, 1900, cxxx., 1322) found that a vigorous action ensues when magnesium powder is added to a mixture of methyl iodide and anhydrous ether. The magnesium gradually dissolves with the formation of a clear solution from which, on evaporation of the ether, a crystalline grey hygroscopic solid is obtained. If an aldehyde (1 mol.) is added to the ethereal solution obtained from magnesium (1 mol.) and methyl iodide (1 mol.), a vigorous action again takes place with the formation of a magnesium organic compound, which, when decomposed by dilute acid, gives a good yield of the corresponding secondary alcohol.

Grignard found it possible by this method to obtain from benzaldehyde, for example, a satisfactory yield of phenyl-methylcarbinol (*Annales de l'Université de Lyon*, 1901, vi., 1), and the action is represented in the following manner:—

$$CH_3I + Mg = CH_3MgI$$

$$CH_3MgI + C_6H_5.CHO = C_6H_5.CH(OMgI).CH_3$$

$$C_6H_5.CH(OMgI).CH_3 + H_2O = = C_6H_5.CH(OH).CH_3 + MgIOH.$$

Ketones, in an analogous manner, are readily converted into tertiary alcohols; thus Grignard obtained phenyl-dimethylcarbinol from acetophenone:—

$$CH_3I + Mg = CH_3MgI$$

$$CH_3MgI + CH_3.CO.C_6H_5 = (CH_3)_2C(OMgI).C_6H_5$$

$$(CH_3)_2C(OMgI).C_6H_5 + H_2O = = (CH_3)_2C(OH).C_6H_5 + MgIOH.$$

In his first paper Grignard also points out that other

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

alkyl halides may be substituted for methyl iodide with equally satisfactory results.

The successful application of the new reagent for the synthesis of alcohols from esters of aliphatic monobasic acids was described in the following year (*Comptes Rendus*, 1901, cxxxii., 336). Formic esters are converted into secondary alcohols; for example, diethylcarbinol is obtained in a 73 per cent yield from magnesium ethyl bromide and ethyl formate :—

$$C_2H_5Br + Mg = C_2H_5MgBr$$

$$C_2H_5MgBr + H.COOC_2H_5 = H.C(OMgBr)(C_2H_5)(OC_2H_5)$$

$$H.C(OMgBr)(C_2H_5)(OC_2H_5) + C_2H_5MgBr =$$

$$= H.C(OMgBr)(C_2H_5)(C_2H_5) + Mg(OC_2H_5)Br$$

$$H.C(OMgBr)(C_2H_5)(C_2H_5) + H_2O = H.C(OH)(C_2H_5)(C_2H_5) + MgBrOH.$$

Acetic esters, on the other hand, yield tertiary alcohols; for example, trimethylcarbinol is obtained in an 82 per cent yield from methyl acetate :—

$$CH_3MgI + CH_3.COOCH_3 = CH_3.C(OMgI)(CH_3)(OCH_3)$$

$$CH_3.C(OMgI)(CH_3)(OCH_3) + CH_3MgI = CH_3.C(OMgI)(CH_3)(CH_3) + Mg(OCH_3)I$$

$$CH_3.C(OMgI)(CH_3)(CH_3) + H_2O = CH_3.C(OH)(CH_3)(CH_3) + MgIOH.$$

Tertiary alcohols may also be obtained from acid chlorides or acid anhydrides, the action of the magnesium alkyl halide again being assumed to take place in two phases (Tissier and Grignard, *Comptes Rendus*, 1901, cxxxii., 683). Acetyl chloride, for instance, is readily converted into trimethylcarbinol :—

$$CH_3MgI + CH_3.COCl = CH_3.C(OMgI)(CH_3)(Cl)$$

$$CH_3.C(OMgI)(CH_3)(Cl) + CH_3MgI = CH_3.C(OMgI)(CH_3)(CH_3) + MgICl$$

$$CH_3.C(OMgI)(CH_3)(CH_3) + H_2O = CH_3.C(OH)(CH_3)(CH_3) + MgIOH.$$

It was subsequently shown that aromatic halogen compounds behave like alkyl halides in forming magnesium organic compounds (*Comptes Rendus*, 1901, cxxxii., 1182). Thus phenyl bromide forms the compound C_6H_5MgBr, which, by its interaction with methyl benzoate, gives a theoretical yield of triphenylcarbinol. When magnesium phenyl bromide, however, acts on acetyl chloride, diphenylethylene, $(C_6H_5)_2C:CH_2$, is obtained in place of the alcohol $(C_6H_5)_2C(OH).CH_3$.

It was at once appreciated by students of organic chemistry that science was indebted to the French investigator for the discovery of a reagent of more than ordinary importance for synthetic purposes. As is well known, the classical work of E. Frankland and Duppa on zinc alkyl compounds opened up a highly fruitful field of research, to which important contributions were made by Wagner, Butlerow, and Saytzew. Zinc alkyl compounds are, however, difficult to manipulate on account of their spontaneous inflammability, and to this factor the comparatively limited extent of their application may be ascribed. Many of the reactions in which they play a part require weeks, or even months, for their completion, and the yields of the resulting compounds are often far from satisfactory. Magnesium organic compounds, on the other hand, are so much more easily prepared than zinc alkyl compounds; they are not inflammable on exposure to the atmosphere, and they can be manipulated with such facility that the older methods, depending on the use use of zinc compounds, have been superseded. Not only is this the case, but Grignard's reagent has been applied for the preparation of carbon compounds by methods which earlier investigators did not have at their disposal.

Grignard was not the first to attempt the substitution of magnesium alkyl for zinc alkyl compounds for synthetic purposes. Fleck (*Annalen*, 1893, cclxxvi., 134; compare Löhr, *Annalen*, 1890, cclxi., 72), working in Lothar Meyer's laboratory, showed in 1893 that magnesium methyl interacts with acetyl chloride to form trimethylcarbinol; but, in spite of the reactivity of magnesium methyl, the method presented no advantages over the use of zinc alkyls; in fact it was less convenient, since magnesium alkyls are neither volatile nor soluble in the ordinary organic solvents.

In a paper which paved the way for the Grignard reaction, Barbier (*Comptes Rendus*, 1899, cxxviii., 110) showed that the zinc in Saytzew's reaction may be replaced by magnesium, and that it is not necessary actually to isolate magnesium methyl in order to use it subsequently for synthetic purposes. It was possible to obtain dimethylheptenol, $(CH_3)_2C:CH.CH_2.CH_2.C(OH)(CH_3)_2$, from methylheptenone. $(CH_3)_2C:CH.CH_2.CH_2.CO.CH_3$, by adding methyl iodide to an ethereal solution of the ketone in the presence of magnesium.

Grignard (*Revue Générale des Sciences*, 1903, xiv., 1041) was led to study magnesium organic compounds in consequence of this work of Barbier, and of an observation of E. Frankland and Wanklyn that the zinc compound $Zn(CH_3)_2,(C_2H_5)_2O$ is formed when methyl iodide is heated with zinc and anhydrous ether in a sealed tube.

In the present account of Grignard's action the more important applications will be indicated, but no attempt will be made to give a complete *résumé* of all the work carried out in this field. Section I. deals with the various types of synthesis accomplished by aid of Grignard's reagent, Section II. with some practical details, and Section III. with the theoretical aspect of the subject.

Section I.

Alcohols and Phenols.

(*a*) *Secondary Alcohols.*—A large number of secondary alcohols have been obtained from aldehydes or from formic esters by the method already indicated in the Introductory Section.

(*b*) *Tertiary Alcohols.*—The mode of formation of tertiary alcohols from ketones, acid chlorides, acid anhydrides, and esters respectively has also been referred to. A large amount of work has been done in this particular branch, not only by Grignard himself, but, amongst others, by Acree, Béhal, Klages, W. H. Perkin, jun., Sachs, and Zelinsky.

Cyclic ketones behave normally towards Grignard's reagent; thus Zelinsky (*Ber.*, 1902, xxxv., 2683), converted *cyclo*pentanone, $CH_2.CH_2 > CO$ (with $CH_2.CH_2$), into methyl (1)-*cyclo*pentanol (1), $CH_2.CH_2 > C(OH)(CH_3)$ (with $CH_2.CH_2$), by means of magnesium methyl iodide. As an example of the application to a cyclic ester, Perkin's synthesis of terpineol, $CH_3.C=CH.CH_2>CH.C(CH_3)_2.OH$, from ethyl Δ^2-tetrahydro-*p*-toluate, $CH_3.C=CH.CH_2>CH.COOC_2H_5$, may be quoted (*Trans. Chem. Soc.*, 1904, lxxxv., 654).

Tertiary alcohols are also obtained by other methods of less importance for preparative purposes. Grignard

(*Comptes Rendus*, 1904, cxxxviii., 152; *Bull. Soc. Chim.*, 1904, [3], xxxi., 751) showed that when an ethereal solution of a magnesium alkyl halide is saturated with carbon dioxide, and the product then boiled with an excess of the reagent, trialkylcarbinols are obtained :—

$$RMgX + CO_2 = R.COOMgX$$

$$R.COOMgX + 2R'MgX = \begin{matrix} R \\ R' \\ R' \end{matrix}\!\!>\!C.OMgX + MgO + MgX_2$$

$$\begin{matrix} R \\ R' \\ R' \end{matrix}\!\!>\!C.OMgX + H_2O = \begin{matrix} R \\ R' \\ R' \end{matrix}\!\!>\!C.OH + Mg\!<\!\begin{matrix} OH \\ X \end{matrix}.$$

As will be pointed out later, a general method for making carboxylic acids is to pass carbon dioxide through the Grignard reagent and then decompose the product by water; thus Zelinsky describes the elegant method of obtaining benzoic acid by the action of carbon dioxide on magnesium phenyl iodide (*Ber.*, 1902, xxxv., 2692) :—

$$C_6H_5I + Mg = C_6H_5MgI$$

$$C_6H_5MgI + CO_2 = C_6H_5.COOMgI$$

$$C_6H_5.COOMgI + H_2O = C_6H_5.COOH + MgIOH.$$

But this type of action is not always so simple. Schroeter (*Ber.*, 1903, xxxvi., 3005; compare Meyer and Tögel, *Annalen*, 1906, cccxlvii., 55) substituted phenyl bromide for the iodide in the making of the Grignard reagent, which with carbon dioxide gave triphenylcarbinol as the main product, whilst benzoic acid and benzophenone were also obtained. In fact, the experimental conditions may be so adjusted that no benzoic acid is obtained at all (*Ber.*, 1907, xl., 1584). The formation of triphenyl carbinol is represented as follows :—

$$C_6H_5MgBr + CO_2 = C_6H_5.COOMgBr$$

$$C_6H_5.COOMgBr + C_6H_5MgBr = \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C\!<\!\begin{matrix} OMgBr \\ OMgBr \end{matrix}$$

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C\!<\!\begin{matrix} OMgBr \\ OMgBr \end{matrix} + C_6H_5MgBr =$$

$$= \begin{matrix} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C.OMgBr + MgO + MgBr_2$$

$$\begin{matrix} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C.OMgBr + H_2O = \begin{matrix} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C.OH + MgBrOH.$$

Tertiary alcohols may also be obtained directly from carboxylic acids by the action of an excess of the Grignard reagent (Farbenfabriken vorm F. Bayer and Co., D.R.-P., 1906, 166898); thus phenyldiethylcarbinol, $C_6H_5(C_2H_5)_2C.OH$, is formed from benzoic acid and magnesium ethyl bromide. Metallic salts of carboxylic acids may be applied in a similar manner (*Ibid.*, 1906, 166899), thus trimethylcarbinol is formed from potassium acetate and magnesium methyl iodide.

The synthesis of tertiary amino-alcohols from esters of amino-acids has been studied more particularly by Paal (*Ber.*, 1905, xxxviii., 1686; compare *Ber.*, 1906, xxxix., 810, 2062, 4344). For example, magnesium phenyl bromide and ethyl glycollate, $NH_2.CH_2.COOC_2H_5$, form diphenylhydroxyethylamine, $NH_2.CH_2.C(OH)(C_6H_5)_2$.

After Houben (*Ber.*, 1904, xxxvii., 489) had shown that lactones when acted on by the Grignard reagent give tertiary alcohols, Paal and Hörnstein (*Ber.*, 1906, xxxix., 1361, 2823, 2827) prepared 1 : 1 - diphenyl-*d*-sorbitol, $CH_2OH.(CHOH)_4.C(OH)(C_6H_5)_2$, by acting on the acetyl derivative of *d*-gluconic lactone with magnesium phenyl bromide.

A very convenient method for preparing ditertiary glycols was employed by Valeur, who acted on esters of dicarboxylic acids with an excess of the Grignard reagent (*Comptes Rendus*, 1903, cxxxvi., 694; *Bull. Soc. Chim.*, 1903, xxix., 683; compare Dilthy and Last, *Ber.*, 1904, xxxvii., 2639); in this manner methyl oxalate and magnesium phenyl bromide yield benzpinacone, $(C_6H_5)_2C(OH).C(OH)(C_6H_5)_2$. Ditertiary glycols may also be obtained either from esters of ketonic acids or from diketones; thus Grignard (*Comptes Rendus*, 1902, cxxxv., 627) obtained the glycol $CH_3.C(OH)(C_5H_{11}).CH_2.CH_2.C(OH)(C_5H_{11})_2$ from magnesium *iso*amylbromide and ethyl levulate, $CH_3.CO.CH_2.CH_2.COOC_2H_5$; whilst Zelinsky (*Ber.*, 1902, xxxv., 2138) obtained the pinacone,—

$$(CH_3)_2.C(OH).C(OH)(CH_3)_2,$$

from diacetyl, $CH_3.CO.CO.CH_3$, and magnesium methyl iodide.

Acree (*Ber.*, 1904, xxxvii., 2753) shows that the action with a diketone may be regulated so that either one or both of the carbonyl groups react. It is possible, for example, to obtain from benzil, $C_6H_5.CO.CO.C_6H_5$, either the keto-alcohol, phenylbenzoin, $(C_6H_5)_2C(OH).CO.C_6H_5$, or benzpinacone, $(C_6H_5)_2C(OH).C(OH)(C_6H_5)_2$.

The optically active glycol, tetraphenylerythritol, $(C_6H_5)_2C(OH).CH(OH).CH(OH).C(OH)(C_6H_5)_2$, has been obtained by P. F. Frankland and Twiss by the action of magnesium phenyl bromide on dimethyl *d*-tartrate (*Trans. Chem. Soc.*, 1904, lxxxv., 1666).

(*c*) *Primary Alcohols.*—The Grignard reagent is not so useful for the preparation of primary alcohols as for the classes to which reference has been made. When a current of dry oxygen is passed into an ethereal solution of the Grignard reagent, oxidation takes place and a primary alcohol is formed when water is added (Bouveault, *Bull. Soc. Chim.*, 1903, [3], xxix., 1051), *e.g.*,—

$$C_6H_5.CH_2MgCl + O = C_6H_5.CH_2OMgCl$$

$$C_6H_5.CH_2OMgCl + H_2O = C_6H_5.CH_2OH + MgClOH,$$

the yield of benzyl alcohol being 80 per cent.

When the Grignard reagent is heated for several days with trioxymethylene the primary alcohols are obtained, sometimes in good yield; thus *n*-propyl alcohol is obtained from magnesium ethyl bromide (Grignard and Tissier, *Comptes Rendus*, 1902, cxxxiv., 107).

Ethylene oxide may also be converted into primary alcohols (Blaise, *Comptes Rendus*, 1902, cxxxiv., 551), for example, *n*-butyl alcohol is obtained from magnesium ethyl bromide (Grignard, *Comptes Rendus*, 1903, cxxxvi., 1260; *Bull. Soc. Chim.*, 1903, [3], xxix., 944).

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!O + Mg\!<\!\begin{matrix} C_2H_5 \\ Br \end{matrix} = \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!O\!<\!\begin{matrix} C_2H_5 \\ MgBr \end{matrix} \rightarrow$$

$$\rightarrow C_2H_5.CH_2.CH_2.OMgBr \rightarrow C_2H_5.CH_2.CH_2OH.$$

The action of ethylene monochlorhydrin on a magnesium organic compound takes place in two phases. The hydroxy-group is first acted on in the cold :—

$$RMgX + CH_2Cl.CH_2OH = RH + CH_2Cl.CH_2OMgX.$$

On the addition of a second molecular proportion, R'MgX, which may be different from the first, a vigorous reaction again takes place when the ether is distilled off from the mixture and the temperature gradually raised :—

$$R'MgX' + CH_2Cl.CH_2OMgX =$$

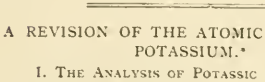
$$= MgX'Cl + R'.CH_2.CH_2.OMgX.$$

Phenylethyl alcohol, $C_6H_5.CH_2.CH_2OH$, is readily obtained in this manner from magnesium phenyl bromide (Grignard, *Comptes Rendus*, 1905, cxli., 44; *Bull. Soc. Chim.*, 1907, [3], x., 23).

(*d*) *Phenols.*—Bodroux (*Comptes Rendus*, 1903, cxxxvi., 158; *Bull. Soc. Chim.*, 1904, [3], xxxi., 33) applied for the preparation of phenols the method which Bouveault used for primary alcohols (*loc. cit.*), but the yields obtained were very small. The method appears, however, to be a general one. Thiophenols and selenophenols are formed in an analogous manner (Wuyts and Cosyns, *Bull. Soc. Chim.*, 1903, [3], xxix., 689; Taboury, *Ibid.*, 1904, [3], xxxi., 1183).

The action on *p*-quinones has been investigated by Bamberger and Blangey (*Ber.*, 1903, xxxvi., 1625), who

obtain quinols, but in small yield. Werner and Grob (*Ber.*, 1904, xxxvii., 2892) find that phenanthrene quinone and magnesium phenyl bromide give 9 : 10-dihydroxy-diphenyldihydrophenanthrene,—



(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF POTASSIUM.*

I. The Analysis of Potassic Chloride.

By THEODORE WM. RICHARDS and ARTHUR STAEHLER.

(Concluded from p. 136).

The Drying and Weighing of the Potassic Chloride.

The final preparation of the salt for analysis is given a special chapter to itself, because the proper execution of this feature is of very great importance, not less than the purification of the material. It is clearly useless to separate 0·001 per cent of a metallic impurity if 0·01 per cent of water is allowed to remain in the salt.

Obviously, superficial drying can not remove the imprisoned moisture in the crystals, hence they must be fused (Richards, *Zeit. Phys. Chem.*, 1903, xlvi., 189). Except in a few preliminary experiments, where a common platinum crucible was used, this fusion was conducted in a platinum boat or open bottle contained in a porcelain tube through which a current of nitrogen was passing. The experience in a number of similar cases, that the simultaneous presence of oxygen and traces of hydrochloric acid enclosed in the crystals is likely to cause perceptible corrosion of the platinum boat, was confirmed in this case; hence, an inert gas was needed. The nitrogen was prepared by the well-known method of Wanklyn, by passing air charged with ammonia over red hot copper. The excess of ammonia was carefully eliminated by washing the gas with much dilute acid. Because fused sodic chloride was found to be essentially free from dissolved nitrogen, we did not think it necessary to fuse this very similar potassium salt in a vacuum.

Potassic chloride, although not so hygroscopic as some other salts, used in similar researches, is, nevertheless, far too hygroscopic to weigh safely when directly exposed to the air of the balance room. Its tendency to attract water was seen in perceptible crackling when the tube containing fused salt was opened in the moist atmosphere of the beaker to be used for the solution of the salt.

At first the bottling apparatus so often used in the Chemical Laboratory of Harvard College was employed to protect the fused chloride from moisture during the determination of its weight, the chloride being contained in a platinum boat protected by a glass-stoppered weighing bottle. Because, however, the weighing room was not wholly constant in temperature or in moisture, time and trouble were needed to obtain exact weighings, even although the apparatus was always weighed by substitution against a similar empty boat and bottle. The use of quartz weighing bottles proved to be no advantage, indeed, if anything, a disadvantage. In either case, if time enough were taken, satisfactory weighings could be made; but as time was especially precious, another device was used which wholly overcame the trouble.

This effective and satisfactory device consisted in the use of small weighing bottles of platinum, shaped like the long Lawrence Smith crucible, which were closed by small platinum capsules, fitting into the bottles like ground stoppers. One of these bottles, containing the potassic chloride, was supported by a loop of platinum wire in an inclined porcelain tube, and above it in the tube was placed its platinum stopper. Glass stoppers fitted into each end of the porcelain tube, which was encircled by a suitable furnace. After the potassic chloride had been dried for a long time at a high temperature, just barely fused in nitrogen, and cooled in a current of pure dry air, the stopper was shaken into place and the platinum bottle quickly removed and placed in a desiccator. This arrangement is essentially similar to the bottling arrangement of Richards and Parker, except for the additional advantages that glass is wholly eliminated and that the enclosed air-volume in the tube is much smaller. Probably the burnished platinum joint is not as tight as the ground-glass joint; but it is amply tight enough to prevent any appreciable diffusion of moisture during the very brief exposure of the tube. This was evident from the constancy of the weighings, which were made by substitution against a similar empty platinum bottle kept in a similar desiccator. The weighings were very quickly performed and were trustworthy. Before being used, the platinum bottles were repeatedly ignited with pure sublimed ammonic chloride in order to remove iron; they remained satisfactorily constant in weight during subsequent experiments, the one used for the fusion losing only 0·3 mgrm. in fourteen experiments, or on the average 0·02 mgrm. in a single experiment. In one experiment, where oxygen was present during the fusion, as much as 0·3 mgrm. was taken from the boat, the platinum being plainly visible on solution. This was, of course, not used for analysis.

All weighings, whether of this salt or of silver or argentic chloride, were made by substitution in the manner already described in other papers. (For example, see Richards and Rogers, *Zeit. Anorg. Chem.*, 1895, x., 19; also Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 465). The balance was a short-armed instrument made by Troemner, of the type adopted in other similar investigations; it was used only for this work and that to be described afterward. The weights were of platinised brass, carefully standardised according to the usual Harvard method. (Richards, *Journ. Am. Chem. Soc.*, 1900, xxii., 144; these weights had an average density of 8·3).

All weighings were reduced to the vacuum standard. Thus, from every apparent grm. of silver, 0·00003 grm. was subtracted, and to every apparent grm. of argentic chloride, 0·000071 was added, if the temperature was 20° and the pressure normal. Assuming the density of potassic chloride to be 1·995, the similar correction for this salt was +0·000456. Changes in temperature and pressure occasionally caused slight but usually inessential changes in these corrections (Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 465).

The wholly colourless transparent fused salt was dissolved in the purest water in a covered beaker of Jena glass under a tightly fitting bell-jar. The solution was always perfectly clear, except in the rejected case already cited and one other similar one. After this solution had been very thoroughly washed away and used for analysis, the platinum weighing bottle was heated for a short time in another crucible, and weighed in preparation for another analysis. The constancy of these weighings has already been discussed.

The details of preparation having been described, the analytical methods themselves must be indicated. The problem was, as in the case of sodium, to determine the amount of chlorine present, the weight of potassium being found by difference. Both of the previously used methods for finding the amount of chlorine were used, and the details are so much like those discussed by Richards and Wells (*loc. cit.*) that much may be assumed as understood. For a full understanding of the present work, that upon sodium should be read in connection with it.

The two methods for the determination of chlorine, namely, the weighing of the precipitated argentic chloride on the one hand, and the discovery of the equivalent amount of silver on the other, are discussed below in order,

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The Precipitation and Weighing of Argentic Chloride.

For purposes of analysis, the solution of potassic chloride was carefully and completely transferred to a large Jena glass Erlenmeyer flask with a finely ground glass stopper, and diluted to the volume of a litre or more. To this in the dark-room under the red light was added exactly the calculated weight of argentic nitrate, never more concentrated than one-fiftieth normal; and the mixture was shaken for a short time in order to aggregate the great mass of the precipitate. Because of the absence of an excess of argentic nitrate, the danger of the occlusion of this salt was slight. On the following day the supernatant liquid was usually quite clear, and to it now was added the excess of perhaps 0·05 grm. of argentic nitrate needed for complete precipitation. This method of treatment was found to be more satisfactory than the immediate addition of all the argentic nitrate at once, as in this case long and tiresome shaking and washing of the precipitate was needed to eliminate wholly the occluded argentic nitrate. Thus was one of the chief difficulties met by previous experimenters almost entirely overcome. It was shown in the paper on sodium that the simplest test for the presence of argentic nitrate is the appearance of the argentic chloride after fusion, even a small trace of nitrate causing a perceptible grey-violet cloudiness. In all cases when the above precaution was used the fused mass was perfectly clear and transparent. This is, however, an anticipation of the later part of the process; the collection, ablution, and desiccation of the precipitate should first be described.

In preliminary experiments, the Gooch perforated platinum crucible with asbestos mat was used with all the precautions previously adopted in this laboratory. In this way it is certain that good results may be obtained; but the necessary second filtration of the filtrate in order to collect the traces of disintegrated asbestos is a tiresome process. On this account preliminary experiments were made with Gooch crucibles provided with a smooth and burnished mat of platinum sponge, as prepared by Heraeus. (See *Zeit. Angew. Chem.*, 1901, xiv., 923; a number of experimenters have recommended and used a mat of platinum sponge in a Gooch crucible, but Munroe was probably the first, *Journ. Analyst Chem.*, 1888, ii., 241; also CHEMICAL NEWS, 1885, lviii., 101). Such crucibles are named by him after Neubauer, but might more properly be called Gooch-Munroe crucibles. In these tests it was found that such crucibles, as a matter of fact, answer very well for the purpose in hand if certain special precautions are taken. It is not permissible to ignite them at a high temperature, unless the precipitate also is to be ignited at a high temperature. A crucible brought to constant weight at 150° was found to lose 0·15 mgrm. on ignition, probably because of loss of previously adsorbed water. Moreover, when a dilute solution of argentic nitrate, potassic nitrate, and nitric acid, such as remains after an analysis, was passed through the filter, and this was five times washed with water, and dried at 150°, yet 0·15 more was gained, probably due to adsorbed salts. Very thorough washing after this brought the crucible back to its original weight after drying at 150°.

These experiments showed that the washing of the platinum sponge must be very thorough, and that a definite temperature must always be used for drying. Other experiments showed that constant weight could always be obtained, if these conditions were fulfilled.

It is well known that argentic chloride sometimes clings to a platinum surface, and always shrinks much on drying. On this account the somewhat delicate upper surface of the sponge was protected by a closely fitting disk or diaphragam of platinum punched with many fine holes. This diaphragm, merely laid upon the top of the sponge at the base of the crucible, was easily loosened with the precipitate, and formed an effectual protection for the sponge. After this was done, no platinum was ever lost from the upper surface, and none was ever carried away mechanically from below in the wash-water.

In spite of the presence of the disk, small particles of argentic chloride always clung here and there to the sponge. As a possible means of removing these when preparing for a new analysis, potassic cyanide was tested. It was found, however, that not only was this salt adsorbed by the sponge, but that in the presence of air platinum was dissolved even to the extent of a mgrm.—a fact not new, but none the less pertinent. Thiosulphate was not tried, because sulphur was an impurity little wished. Finally, while ammonia for a short time was inefficient, this liquid, when concentrated and applied for twelve hours or more, dissolved every trace of the silver salt without harming the crucible.

The technique of the Gooch-Munroe crucible having thus been mastered, this utensil was used with satisfaction as a means of collecting and weighing the precipitate in hand. The latter was first washed often by decantation, as is recounted below, and finally on the filtering crucible, which was dried to constant weight by a temperature gradually rising to 150°. After careful weighing, the main mass was separated from the clinging platinum disk, and was carefully fused in porcelain, as has often been described. The accurately determined loss on fusion, amounting sometimes to a mgrm., was calculated from the part to the whole, and applied as a correction to the total weight of the precipitate.

This weight, even as thus corrected, did not, however, exactly represent the total in weight of the chlorine, as some of the argentic chloride was dissolved by the wash-water. The ablution had been conducted in three stages, just as in the often-cited investigation of sodium. The first stage included the mother-liquor and first five wash-waters, containing intentionally as much argentic nitrate as the mother-liquor, and added to remove the greater part of the potassic nitrate. This first quantity of liquid was entirely free from chlorine in every accepted analysis, as was shown by careful testing in the nephelometer, and so was at once cast aside.

The second stage of washing was conducted with very dilute nitric acid, and yielded 0·5 or 0·6 litre of a very dilute solution of mixed nitric acid and argentic chloride and nitrate. The traces of chloride which it contained were carefully estimated in the nephelometer after addition of excess of argentic nitrate.

The third stage of the washing, also conducted with pure water acidified with nitric acid to prevent colloidal irregularities, yielded a litre or more of liquid containing much argentic chloride. The analysis of this liquid constituted a very important part of the work and gave much trouble.

In order to be as certain as possible of the weight of chlorine it contained, this liquid was tested in five cases according to two very different methods. The first of these consisted in evaporation of the solution under diminished pressure and actual weighing of the precipitate, and the second consisted in a new modification of the nephelometer test. Although the latter evidently gave the more satisfactory results, the former is worthy of brief discussion, because its outcome certainly represents the maximum value.

In order to carry out these two parallel quantitative tests, the collected wash-water was divided into two parts; and the larger part, about 90 per cent of the whole, was evaporated under low pressure at 50° in a specially made Jena glass 2-litre flask with a glass stopper. In the course of this evaporation the argentic chloride began to separate out when the volume had been reduced to about 0·2 litre, if 2 mgrms. of the salt were present—a fact agreeing well with the recent observations concerning this solubility (see, for example, Bottger, *Zeit. Phys. Chem.*, 1906, lvi., 93). The dried residue was dissolved in a very little ammonia freshly distilled in platinum, and washed into a small precipitating flask, where it was re-precipitated with excess of argentic nitrate and nitric acid. This trace of precipitate was collected and weighed on a fresh Gooch-Munroe crucible in the same way as the larger mass. The results

are given below in comparison with those obtained from the same solutions by the nephelometer.

An important modification was introduced into the nephelometric determination. One of us has repeatedly pointed out that in order to obtain satisfactory results with this instrument the solution to be tested and that used as the standard of comparison must be treated in exactly the same way (*Am. Chem. Journ.*, 1904, xxxi., 242; 1906, xxxv., 509). Hence, the use of a ground-glass plate as a standard of comparison is a very questionable proceeding (Wells, *Am. Chem. Journ.*, 1906, xxxv., 99). It appears that the precipitation of argentic chloride from solutions of this salt differ perceptibly in mechanism from the precipitation of the same substance from other chloride solutions, even when argentic nitrate in great excess is used in each case (Richards and Wells, *Pub.* 28 Carnegie Inst., 1905, xxviii., *Journ. Am. Chem. Soc.*, 1905, xxvii., 485). Accordingly, in order to secure a perfectly satisfactory comparison, both precipitates must be dissolved in ammonia and re-precipitated. The precipitate then appears in each case in precisely the same condition, and yields trustworthy results.

The present tests were carried out in the following manner:—Two test-tubes of precisely the same volume (0·025 litre) were provided. Into one of these was placed 0·015 litre of the wash-water, and into the other, serving as the standard of comparison, a like volume of water containing about as much carefully measured chlorine (in the form of potassic chloride) as was present in the first. Into each was now run 5 molecules of a three-hundredth normal solution of argentic nitrate. The solutions were stirred with a platinum stirrer, previously cleansed with ammonia and the purest water. After five minutes, the precipitates were well formed; they were then both dissolved with the help of a millilitre of freshly distilled ammonia, and re-precipitated with a slight excess of nitric acid, being filled to similar marks near the top of the tubes. The two cloudy solutions, thoroughly stirred, were allowed to stand and compared optically in the nephelometer in the usual way.

The following table compares the results obtained by the two methods. The varying solubility of the halide in the wash-water was mainly due to difference in temperature at the time of the ablution.

The Comparison of Weights of Argentic Chloride found Nephelometrically and by Evaporation.

Experiment No.	Volume.	Weighs of argentic chloride. By evaporation.	By nephelometer.	Diff.
	Litres.	Mgrms.	Mgrms.	Mgrm.
10.	1·45	3·96	3·12	−0·84
11.	1·88	3·82	3·22	−0·60
12.	1·18	2·59	1·97	−0·62
13.	0·90	1·70	1·35	−0·35
14.	1·00	1·74	1·45	−0·29

Thus, the nephelometer always indicated less argentic chloride than the gravimetric process. At first the nephelometer was suspected, but the steadily diminishing difference between the two series of results indicated that they were approaching the point where they would indicate the same values. As the nephelometric treatment was invariable, but, on the other hand, the evaporating flask might easily be attacked, it seemed probable that the decreasing difference exhibited by the figures was due to something added to the weight of the precipitate from the latter source. Apparently, as is reasonable, the flask was less and less attacked as it continued in use.

For this reason the gravimetric results were wholly rejected, and the nephelometric ones alone used in the calculation of the final results.

The Ratio of Potassic to Argentic Chloride.

The final results of the series of analyses discussed above are recorded in the following table. A number of preliminary experiments are omitted from this table, since it is clear that no doubtful or imperfectly executed experiment should find a place in such a table of final data. The list is nearly consecutive, however, as but few experiments met with misfortune after the processes had been mastered. The original numbering of the experiments is retained; they were recorded in the notebook in chronological order. All the argentic chloride referred to in this table was clear and colourless; a fact which is one of the best proofs that it was free from argentic nitrate or from organic dust.

Final Series of Determinations of the Ratio KCl : AgCl.

No. of analysis.	Preparation of KCl.	Weight of fused KCl in vacuum.	Weight of fused AgCl in vacuum.	AgCl : KCl = 100·000 : x.	Atomic weight K if Cl = 35·473.
		Grms.	Grms.		
13.	*a*	4·36825	8·3986	52·012	39·114
14.	*a*	5·56737	10·7038	52·013	39·115
15.	*a*	6·41424	12·3323	52·012	39·114
20.	*b*	3·27215	6·2913	52·011	39·112
31.	*b*	4·83028	9·2870	52·011	39·112
		Average		52·0118	39·1134

This result will be discussed after the next series has been presented. It has a probable error, calculated by the method of least squares, of only about 0·0004; accordingly, further repetition was deemed unnecessary.

The Ratio of Potassic Chloride to Silver.

In this series of experiments, weights of the purest silver equivalent to entirely new portions of fused potassic chloride, as calculated from the preceding table, were dissolved in nitric acid, and the two equivalent solutions were mixed. Great care was used. The presence of an excess of silver or of chlorine was then determined with the nephelometer, exactly according to the details of manipulation adopted by Richards and Wells, whose accounts should be consulted for particulars. The table below contains the final results; the preliminary practice experiments are omitted for the same reason as before.

Final Series of Determinations of the Ratio Ag : KCl.

No. of analysis.	Preparation of KCl.	Weight KCl in vacuum.	Weight Ag in vacuum.	Ratio Ag:KCl = 100·000:x.	At. wt. of K if Cl = 35·473.
		Grms.	Grms.		
19.	*a*	3·88074	5·61536	69·109	39·117
21.	*a*	7·44388	10·77156	69·107	39·114
24.	*c*	5·00681	7·24514	69·106	39·113
27.	*e*	5·04833	7·30515	69·107	39·114
30.	*e*	8·19225	11·85412	69·109	39·117
32.	*d*	4·99795	7·23230	69·106	39·113
33	*f*	5·16262	7·47042	69·107	39·114
		Average		69·1073	39·1145

In this case the "probable" error is even somewhat less than before, being under 0·0004.

Discussion of Final Results.

Thus, two results have been obtained, giving for the atomic weight of potassium the value 39·113 by reference to argentic chloride, and the value 39·114 by reference to pure metallic silver. The close agreement of these results is an important evidence of their verity, and a striking confirmation of the new atomic weight of chlorine found by Richards and Wells. The atomic weight of chlorine is very simply calculated from the results of the two series above as follows: — Cl = (69·1073 52·0118—1·00000) 107·93 = 35·475—very near the most likely value, 35·473.

Such difference as exists is probably due to the slight remaining trace of occlusion of foreign salts by the argentic chloride. In the present case this source of error was eliminated more successfully than ever before, hence the agreement between the two values of the atomic weight of potassium was closer than usual.

It may be noted that the difference between the new

value and the old value of Stas is somewhat less than in the case of sodium. Stas's results with potassic chloride led him to the value 39·146, about 0·032 higher than the new result, while with sodic chloride the difference was 0·042. A large part of this difference in each case is due to Stas's error in the atomic weight of chlorine; corrected for this error, the differences become 0·016 and 0·026 respectively. The differences are to be referred to the same causes in this case as in the others—namely, to Stas's incomplete knowledge concerning solutions of argentic chloride, to his practice of dropping solid salt into the precipitating solution, and to the presence in his preparations of traces of impurity taken from containing vessels. In the case of potassium one or more of these errors must have been less than in the case of sodium.

The results of Richards and Archibald, although very few in number and not intended to figure in a discussion of this kind, were somewhat better—probably because solid salt was never used directly in precipitation. Assuming the present research to yield the true value, their errors in the two series were, respectively, 0·009 and 0·014. The result of Archibald alone for the ratio of silver to potassium chloride was about the same amount (0·008) different from the present value; but his result for the other ratio was less satisfactory, having an error of 0·021, even greater than Stas's. These differences are not surprising, because less was known at that time than at present concerning the behaviour of argentic chloride in solution.

Although the present paper presents strong evidence that the atomic weight of potassium is really as low as 39·114, more remains to be done. It would have been desirable to have used also some other wholly different method of preparing potassic chloride, and, moreover, to have evaporated large samples of the salt in nitrogen in order to discover a possible non-volatile residue. It is very doubtful if these additional experiments would have altered the present result, especially considering the precautions taken in the work, and the result of the following research; but, nevertheless, it is planned to pursue these matters further.

Even when every conceivable precaution is taken, a single salt is not an adequate basis for the certain decision of an atomic weight. For this reason a parallel investigation on potassic bromide was simultaneously in progress at the Chemical Laboratory of Harvard College. The next communication, describing this other research, must be considered in connection with the work which has just been described. As will be seen, excellent confirmation of the present work is afforded by the work with the bromide.

Summary.

This investigation concerning the quantitative composition of potassic chloride resembled in many respects the recent investigation of Richards and Wells on sodium.

In several details, however, improvements were introduced which effected a considerable saving of time and a perceptible gain in accuracy.

The precautions necessary for the accurate use of the Gooch-Munroe perforated crucible were ascertained; its employment was found to be advantageous.

Platinum weighing bottles with conical ground-platinum stoppers were used instead of boats and glass tubes for weighing the potassium salt.

Occlusion of argentic nitrate by the precipitated chloride was diminished by allowing the latter to stand for a long time in a solution containing neither excess of silver nor excess of soluble chloride, and by adding more argentic nitrate only after the precipitate had assumed a fairly permanent condition of aggregation.

The nephelometric estimation of small amounts of suspended argentic chloride was increased in accuracy by redissolving in ammonia both of the opalescent precipitates to be compared and re-precipitating in order to equalise the conditions.

As final results, the outcome of twelve experiments, 100·000 parts of silver were found to correspond to 52·0118 parts of potassic chloride, and 100·000 parts of argentic chloride were found to correspond to 69·1073 of this salt.

The corresponding values for the atomic weight of potassium (if silver is assumed to be 107·930 and chlorine 35·473) are 39·1134 and 39·1145, in unusually close agreement.

A METHOD FOR THE ESTIMATION OF IRON IN PRESENCE OF TITANIUM.

By F. A. GOOCH and H. D. NEWTON.

FOR analytical purposes, a ferric salt in solution is most easily and conveniently reduced to the ferrous condition by the action of zinc; and where many determinations of iron are to be made, the use of the well-known reductor, first proposed by Jones ("The Chemical Analysis of Iron," Second Edition, p. 203), and described in simple form by Blair ("The Chemical Analysis of Iron," Sixth Edition, p. 94), yields accurate results very rapidly. The use of zinc, whether in the flask or in the reductor, has, however, been precluded when the ferric salt is accompanied by titanic acid, for this substance is reduced with the iron and subsequently oxidised by the permanganate in the titration process. When, therefore, titanium is present with the iron, it has been customary to have recourse to other methods of reduction. In this event, either hydrogen sulphide or sulphur dioxide is substituted for the zinc to bring about the reduction of the ferric salt, while titanic acid is not reduced by these reagents; but the removal of the excess of hydrogen sulphide or of sulphur dioxide from solution without oxidation of the ferrous salt is not an easy or rapid process.

The present investigation was undertaken for the purpose of adapting the ordinary convenient process of reducing the ferric salt by zinc to the estimation of iron in presence of titanium. It is obvious that to solve this problem it is only necessary to find and employ some reagent which shall be neutral toward the ferrous salt but capable of re-oxidising the titanium compounds formed by the reducing action of the zinc and without action on the permanganate. Compounds of silver, copper, or bismuth oxidise very easily the reduced titanium salt; but the use of a compound of silver is precluded by the fact that it oxidises also the ferrous salt to some extent as well as the titanium salt. Cupric salts and pure bismuth oxide prove, however, to be without action upon the ferrous salt.

For the work to be described, ferric oxide was prepared from pure ferrous oxalate and converted to ferric sulphate, and a solution of this salt was made up of convenient strength and standardised by reducing the iron with zinc in a small flask, as recommended by Blair ("The Chemical Analysis of Iron," Sixth Edition, p. 225), and titrating with potassium permanganate. Titanium sulphate was prepared in solution by digesting pure titanic acid in concentrated sulphuric acid and diluting the filtered solution to known volume.

In preliminary experiments it was found that the violet colour of the solution containing the titanium compound produced by the action of zinc upon the titanium sulphate was discharged by adding a little cupric sulphate to the solution and heating, and, after filtering, a drop of potassium permanganate gave its characteristic rose tint to the solution. It was found also that when cupric oxide was added to a similarly reduced solution of the titanium salt the characteristic colour vanished on shaking the solution. The following table contains the results obtained in titrating with potassium permanganate the ferrous salt left after reducing by zinc in small flasks carefully measured amounts of ferric sulphate and titanium sulphate, treating the mixture thus obtained with cupric sulphate or with

cupric oxide, and filtering off the reduced copper and cuprous salt.

TABLE I.

Fe_2O_3 taken.	TiO_2 taken.	Fe_2O_3 found.	Error.	
Grm.	Grm.	Grm.		
0·1375	0·1	0·1378	+0·0003	(a)
0·1375	0·1	0·1374	−0·0001	
0·1375	0·1	0·1377	+0·0002	
0·1375	0·1	0·1378	+0·0003	(b)
0·1375	0·1	0·1378	+0·0003	
0·1375	0·2	0·1382	+0·0007	

(*a*) Treated with $CuSO_4$. (*b*) Treated with CuO.

So it appears that either cupric sulphate or cupric oxide may be used to re-oxidise the salt of titanium reduced by zinc, without affecting appreciably the ferrous salt in solution.

Similar experiments in which bismuth oxide was substituted for the copper oxide are recorded in Table II. To the measured amount of ferric sulphate and titanium sulphate contained in a small flask, provided as usual with the funnel valve, zinc was added, and the reduction effected in the ordinary manner. The titanium salt appears to act catalytically in this process, so that reduction goes on more easily and with less expenditure of zinc than in the similar reduction of the ferric salt taken by itself. After the zinc had disappeared, the solution, of characteristic violet colour, was cooled in the flask, treated with a little bismuth oxide, gently shaken, filtered from the excess of bismuth oxide and the precipitated bismuth into about a litre of cold water, and titrated with standard potassium permanganate.

In Table III. are given the results obtained when reduction was effected by passing the ferric sulphate solution through a column of amalgamated zinc, 20 to 30 mesh, used in the simple form of reductor recommended by Blair (*loc. cit.*). The receiving flask was kept cool in running water, a small amount of bismuth oxide added, the flask shaken, and allowed to stand a few minutes, and filtration made with the aid of the suction pump. In the cold solution free from dissolved oxygen there is little danger of re-oxidation of ferrous sulphate, as has been shown by Peters and Moody (*Am. Journ. Sci.*, xii., 367).

TABLE II.

Ferric sulphate.	TiO_2.	$KMnO_4$.	Fe_2O_3 taken.	Fe_2O_3 found.	Error.
Cc.	Grm.	Cc.			
10	0·04	12·84	0·0993	0·0992	−0·0001
10	0·06	12·85	0·0993	0·0993	0·0000
10	0·08	12·90	0·0993	0·0997	+0·0004
10	0·1	12·90	0·0993	0·0997	+0·0004
10	0·1	12·89	0·0993	0·0996	+0·0003
10	0·1	12·85	0·0993	0·0993	0·0000
10	0·1	12·80	0·0993	0·0989	−0·0004
10	0·1	12·90	0·0993	0·0997	+0·0004
10	0·2	12·90	0·0993	0·0997	+0·0004
10	0·2	12·89	0·0993	0·0996	+0·0003
10	0·2	12·90	0·0993	0·0997	+0·0004
20	0·1	25·70	0·1986	0·1986	0·0000

TABLE III.

40	0·01	46·80	0·3943	0·3943	0·0000
40	0·02	46·79	0·3943	0·3942	−0·0001
40	0·04	46·80	0·3943	0·3943	0·0000
40	0·06	46·83	0·3943	0·3946	+0·0003
40	0·1	46·75	0·3943	0·3939	−0·0004
40	0·1	46·82	0·3943	0·3945	+0·0002
40	0·1	46·78	0·3943	0·3941	−0·0002
40	0·1	46·80	0·3943	0·3943	0·0000
40	0·1	46·75	0·3943	0·3939	−0·0004
40	0·1	46·80	0·3943	0·3943	0·0000
40	0·2	46·77	0·3943	0·3940	−0·0003
40	0·2	46·81	0·3943	0·3944	+0·0001
40	0·2	46·85	0·3943	0·3947	+0·0004

These results show plainly that the ordinary process of reducing ferric salts by means of zinc, either in the flask or in the reductor, may be made applicable in presence of titanium compounds by adding copper oxide or preferably bismuth oxide to the reduced solution, and filtering before titrating with potassium permanganate.—*American Journal of Science*, xxiii., p. 365.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 12, 1907.

New Yttria-niobium Mineral.—Otto Hauser.—The author has analysed a mineral which was described as orangeite, similar to euxenite. Chemical analysis, however, showed that it is a niobate of yttrium, allied in composition to fergusonite, although it differs from the latter in its mineralogical properties and it contains titanic acid and no uranium. It is characterised by its abnormally high loss on ignition. The analysis of the mineral gave the following results:—

Nb_2O_5, TiO_2	45·23
$Y_2O_3, La(Ce,Di)_2O_3$	41·19
Al_2O_3	0·80
Fe_2O_3	2·51
CaO	1·80
PbO	0·19
SnO_2, ThO_2..	Traces
Loss on ignition..	8·40
	100·12

No other elements are present, so that its composition is remarkably simple for a niobate. Among the components of the yttrium earths the colourless earths are predominant, and of the erbium earths dysprosium, and holmium are relatively abundant. Terbium is present only in small quantities, and minute traces only of praseodymium can be detected.

Iodometric Determination of Mercury.—E. Rupp.—The author has already reported that the mercuric ion can be precipitated as metal by alkaline formaldehyde solution and again dissolved by N/10 iodine. The reduction must be carried out at the temperature of the water-bath if the precipitation with alkali is performed directly, while the room temperature is sufficient if the mercury salt is first converted into mercury iodide-potassium iodide by the addition of potassium iodide. The reduction then takes place very quickly, but the liquid has to be thoroughly shaken for one to two minutes. If this is not done, the results obtained are low, because some of the mercury is converted into acetate on acidifying with acetic acid, and it is then incapable of reacting with iodine.

Melting-point of Pure Tungsten.—H. v. Wartenberg.—A satisfactory method of determining the melting-point of tungsten, which is known to lie in the neighbourhood of 3000°, can be carried out with Geissler tubes with Wehnelt's cathode. It is then found that the "black temperature" of tungsten is 2650 ± 20° C., while the true melting-point is at least 2800° C., and probably does not exceed 2850° C. The fused tungsten on cooling looks like highly polished platinum, is easily marked with a knife, but breaks on the application of greater pressure. The density of solid tungsten is greater than that of the fused metal, in which there are interstices.

Separation of Tellurium from the Heavy Metals and the Formation of Cupric Acid.—Bohuslav Brauner and Bohumil Kuzma.—When tellurium is precipitated by sulphurous acid in presence of heavy metals it carries down with it greater or smaller quantities of the following metals:—Mercury, lead, bismuth, copper, cadmium, arsenic, antimony, thallium, &c. From quantitative experiments performed with copper, the authors find that

the amount of copper carried down is greater the greater the amount of it present. Smaller quantities of bismuth and antimony are carried down than of copper. To separate tellurium from the above heavy metals it is best to convert it into the ion TeO_4'' by means of ammonium persulphate, and the telluric acid may then be reduced by means of hydrochloric acid and subsequent precipitation with sulphurous acid, and this method can be employed to separate very small quantities of the heavy metals from tellurium. When the precipitates, containing copper which they have carried down, are oxidised with nitric acid, the solution is evaporated, and the residue taken up with caustic potash, it completely dissolves. If the solution is oxidised with ammonium persulphate, an intense red colouration is produced, which is generally ascribed to cupric acid. Since neither tellurium alone, nor tellurium in presence of another element than copper, gives this red compound on oxidation with persulphate, the unstable cupric acid must be able to exist only as a constituent of a negative complex telluro-cupric acid. Under different conditions salts of the following composition can be prepared:—

$$2K_2O.Cu_2O_3.3TeO_3+xAq,$$
$$2K_2O.CuO.2Cu_2O_3.3TeO_3+xAq.$$

MISCELLANEOUS.

The Sir John Cass Technical Institute.—The new Session will commence on Monday, September 23rd. The work of the several departments has been considerably re-organised since last year. Apart from systematic courses in Physics, Mathematics, and Chemistry, in which provision is made for students preparing for Degrees of London University in Experimental Science, special courses of instruction will be given in Physical Chemistry, Brewing and Malting, and in several branches of Advanced Physics, including Radio-activity. The courses in Physical Chemistry will include General Physical Chemistry, Electro-chemistry, and a laboratory course of practical work; the instruction in Brewing and Malting will also include laboratory work of a technical character, in addition to a course of lectures designed for those engaged in the Brewing and Malting industries, in which full attention will be given to modern methods of work. The teaching in Metallurgy, which for the past four years has formed a distinctive part of the work of the Institute, has now been established as a separate department, and a full graded curriculum, extending over three years, is provided, which includes advanced instruction in the Metallurgy and Metallography of the most important metals and the analysis of Fuel and of Gas for technical purposes, in addition to systematic courses of lectures and laboratory work in general Metallurgy.

Electrical Measuring Instruments.—Messrs. Archibald Constable and Co. beg to announce that they will publish during the autumn a new and comprehensive work on Electrical Measuring Instruments (recorders, meters, &c.), by Mr. Kenelm Edgcumbe, M.I.E.E.

Natural Colour Photography.—The day is close at hand when every camera user will find it as easy to get a perfect picture in colours as it now is to get an ordinary print. The starch grain process, by which this result is put within reach of the least skilful, is the topic of the day in photographic circles, and although the plates themselves are not yet formally on the British market there are a large number of amateurs working the process, and a fine and representative collection will be the feature of the Exhibition of the Royal Photographic Society, just opened at the New Gallery. Over a hundred colour pictures passed through the hands of the Committee, and seventy-two, the work of nineteen exhibitors, have been accepted and hung. The collection will be a revelation to the great body of the public who have not followed the steps by which the process has slowly achieved its present perfection.

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THE CHEMICAL NEWS.

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THE DEPOSITION OF METALLIC SILVER UPON GLASS.

Short Studies in Chemical History (II.).*

By F. D. CHATTAWAY.

Mirrors made of polished metal or of hard polished stone have been known from very early times, and references to them are scattered through ancient literature. The use of glass mirrors with a reflecting surface formed by a coating of gold-leaf, lead, or tin, or even of pitch, is also of considerable antiquity.

Looking-glasses coated with an amalgam of quicksilver and tin first came into use about the middle of the fifteenth century, but it is not known by whom they were originally made. Their manufacture was introduced into Venice in the year 1507, and was carried on with such success that it became an important source of revenue to the Republic, though it is probable that the industry was established earlier in Germany and Flanders.

The actual details of the process used were for long carefully guarded as a trade secret, and the first explicit instruction for carrying it out were given in the middle of the sixteenth century by Johannes Porta, an Italian. He directs that a thin sheet of tin is to be taken and spread carefully on a flat table, a little mercury is to be poured upon it, and rubbed about with a hare's foot till the whole surface is coated and silvery in appearance. On this a clean sheet of white paper is to be laid, and above the paper the carefully cleaned sheet of glass. The paper is then to be drawn out, and the glass pressed down by weights until the excess of mercury has flowed away.

The manufacture of mirrors in this manner did not become well established in Northern Europe till the middle of the eighteenth century, and reached its most extensive development during the latter half of last century.

The operation of coating glass with tin amalgam is still carried out in much the same way. A perfectly smooth sheet of tin-foil, free from all faults and somewhat larger than the glass to be covered, is spread upon a flat well-polished marble or slate slab, and mercury brushed over it till the whole surface is uniformly amalgamated. Wooden laths or glass strips are laid on three sides of the sheet and kept down by weights, while more mercury is added till the tin-foil is covered to a depth of from 4 to 6 mm. A brilliant surface is next produced upon the fluid metal by skimming off the grey coating of oxide with a wooden rod. The sheet of glass, previously very carefully cleaned, is then pushed forward horizontally from one side of the table with its longest edge foremost, so that this edge is always kept dipping below the surface of the mercury, but not touching the tin-foil. By this means the plate is brought into intimate contact with the metal, and dust and air are totally excluded, while if it were let down perpendicularly more or less of both would certainly be enclosed between the glass and the amalgam. To get rid of the excess of quicksilver the upper surface of the glass is next loaded with cast-iron or stone weights covered with flannel or forced down by screws to a pressure of about 1 kgrm. per 7 sq. cm., and the table slightly inclined diagonally. After about four minutes the plate is still more weighted, and allowed to remain thus for twenty-four hours, the inclination being gradually increased to about 10 to 12 degrees. It is then turned over with the coated face uppermost, removed from the table, and gradually raised to an upright position, in which it is kept for three to four weeks. At the end of that time there is left upon the glass a dry hard coating of tin amalgam, which is usually varnished to protect it from accidental damage. The mercury which runs off during the weighting can only be used again after having been completely freed from tin by distillation.

This process takes a long time to complete, and is, moreover, often subject to failure; the plates frequently break under the pressure of the weights, and when they are set vertical drops of mercury sometimes trickle down, producing curved streaks technically called "worms," so that it becomes necessary to re-coat the whole mirror. The amalgam also is liable to become crystalline and is further easily injured by carriage.

The manufacture of mercurial mirrors is attended by the still greater drawback that the workpeople employed very frequently suffer from mercurial poisoning. By strict regulations and the most scrupulous cleanliness this danger can be reduced to a minimum, but it cannot absolutely be guarded against.

At the present time, owing to the invention by various chemists of methods of depositing silver upon glass, mercurial amalgam mirrors are not extensively manufactured, except in France, where the slight yellow tint of silver mirrors is regarded as objectionable.

In England the process is practically given up, and for years the Home Office has not had notified to it a case of mercurial poisoning among mirror makers.

The abandonment of mercurial mirror making with its grave dangers to health affords an excellent illustration of the way in which apparently insignificant chemical discoveries can transform important industries.

When towards the middle of last century the study of organic compounds began to attract widespread attention among chemists, it was soon found that many substances were able to throw down silver from solutions of its salts and form brilliant metallic films on the surface of the glass. Liebig was the first to notice this. In his paper "On the Products of the Oxidation of Alcohol" (*Annalen*, 1835, xiv., 133), announcing the discovery and isolation of the compound which he named aldehyde, he states that if a solution of silver nitrate, to which some drops of ammonia have been added, is warmed with the new compound, the silver oxide is immediately reduced, and that the reduction is accompanied by a peculiar phenomenon, the metal attaching itself to the glass in the form of a thin reflecting layer.

The first attempt to use such a reduction of silver in the manufacture of mirrors was made by Thomas Drayton, of Brighton, who in 1843 protected a process by a patent.

Drayton's specification (A.D. 1843, No. 9968), which is dated November 25th, 1843, states:—"The invention consists in causing silver to be deposited on to glass from a solution of silver by deoxidising the oxide of silver in solution in such a manner that the precipitate of silver will adhere to the glass without any previous coating of the glass with metallic or other substances. I would first remark that the invention is applicable in the manufacture of looking-glass and in other cases where it is desired to have glass coated with silver. It is well known that in silvering glass in the making of looking-glasses, as at present practised by the use of quicksilver, the process is very unhealthy, and it is an important feature in this invention that this injurious and unhealthy process is dispensed with, and the glass is coated with silver deposited from a solution of silver, giving a more beneficial result and a very beautiful effect. My process is as follows:—I take at the rate of one ounce of coarsely pulverised nitrate of silver—that which I generally employ is the lunar caustic of commerce—and mix it with half an ounce of spirits of hartshorn; to these I add two ounces of water, and let the mixture stand twenty-four hours; then filter the same (preserving the deposit on the filter, which is silver). I then add to the filtered liquor three ounces by measure of spirit. I prefer spirits of wine at about 60° above proof, or

* The first of this series, "On the Determination of the Composition of Nitrogen Iodide," appeared in Chemical News, vol. xciv., p. 130.

naphtha. I then add from twenty to thirty drops of oil of cassia. The mixture, after having remained for five or six hours, is ready for use, and I have found it desirable not to keep it more than twenty-four hours after the oil of cassia has been added thereto; but the mixture before the addition of the oil of cassia appears to improve by keeping. When the proper time has elapsed after the addition of the oil of cassia, the mixture is to be applied in the following manner:—The glass intended to be silvered having been placed in a horizontal position, I form a projecting fence at all sides with putty or other suitable material, so that the liquid can cover to a depth of from one-eighth to a quarter of an inch the whole surface of the glass which is to be silvered. The surface of the glass should be clean and polished before pouring on the liquor above described, and when the liquor has been run on to the surface of the glass a few drops, say, from six to twelve, of a mixture consisting of one part by measure of oil of cloves to three parts of spirits of wine, are to be dropped at different places into the liquor on the glass, such six to twelve drops of diluted oil of cloves being the proper quantity for the quantity of liquor above mentioned, or the oil of cloves may be mixed with the liquor just before bringing the same in contact with the glass to be silvered. It should be stated that the more oil of cloves used the more quickly does the deposit of silver take place, but I prefer that the process of precipitation or deposition should take about two hours. . . . I have found that the use of a small quantity of oil of thyme or of carraways varies the colour of the silver, and will be useful in some cases for that purpose. . . . As far as my experience goes, I have found that about 18 grains of nitrate of silver are used for each square foot of glass. . . . As soon as the silver on the glass is perfectly dry, I varnish the back of the silver, and I prefer for such purpose beeswax and tallow in about equal quantities melted together.

"Having thus described the nature of the invention and the means pursued by me in performing the same, I further say that I do not confine myself to the precise details herein described, provided the peculiar character of the invention be retained whereby silver is deposited on to glass from a solution of that metal by deoxidation in such a manner as to cause the silver to adhere to glass without any previous coating of the latter."

This invention of Drayton attracted immediate attention. At a meeting of the Chemical Society held on April 15th, 1844, Robert Warington, who was at that time Secretary, described the process (*Memoirs and Proc. Chem. Soc.*, 1844, ii., 128), and showed a mirror made by it, which evidently impressed the audience, for the admiration excited is mentioned in a rather full account of the meeting given in *Dingler's Polytechnisches Journal* (1884, xcii., 472).

Faraday also lectured upon it at the Royal Institution, and the *Athenæum* of June 15th, 1844, in giving an account of the lecture, which was entitled "On Recent Improvements in the Manufacture and Silvering of Mirrors," says:—"The great subject of the evening was the invention of Mr. Drayton, which entirely dispenses with mercury and tin. By that gentleman's process the mirror is for the first time, literally speaking, 'silvered,' inasmuch as silver is precipitated on it from its nitrate in the form of a brilliant lamina." After describing the method it adds:—"This part of Mr. Faraday's discourse was illustrated by three striking adaptations of Mr. Drayton's process. He (Faraday) first silvered a glass plate the surface of which was cut in a ray-like pattern, then, secondly, a bottle was filled with Mr. Drayton's transparent solution, which afterwards exhibited a cylindrical reflecting surface, and finally a large cell made of two glass plates was placed erect on the table and filled with the same clear solution. This, although perfectly translucent in the first instance, gradually became opaque and reflecting, so that before Mr. Faraday concluded those of his auditors who were placed within view of it saw their own faces, or those of their neighbours, gradually substituted for the faces of those who were seated opposite to them."

Although the mirrors manufactured by Drayton's ingenious device were very beautiful, they never came into actual use, as it was found that they were liable, in the course of a few weeks, to become dotted over with small brownish red spots, which greatly spoiled their appearance.

These spots are due, according to Stenhouse (*Mem. and Proc. Chem. Soc.*, 1844, ii., 242; *Annalen*, 1845, liv., 102), to the fact that the metallic silver, while being deposited on the surface of the glass, carries down with it mechanically small quantities of resinous matter, resulting most probably from the oxidation of the essential oil. In the course of time this resinous matter, which is interposed between the glass and the silver, begins to act on the metallic surface with which it is in contact, and produces small brown spots. Stenhouse noted that if an excess of oil of cloves was employed the flecks appeared much sooner.

This circumstance caused Drayton to modify his process, and in 1848 he took out another patent. The specification (A.D. 1848, No. 12,358) reads:—"My invention consists in causing silver to be deposited on to glass from a solution of silver in such a manner that a precipitate of silver will adhere to the glass without any previous coating being applied, and in order that the invention may be fully understood I will describe the means pursued. I take one ounce of hartshorn, or ammonia, and two ounces of nitrate of silver, three ounces of water, and three of spirit (I prefer spirits of wine), mixing these carefully together. I allow the liquid to stand three or four hours, and then filter it for use. To one ounce of the filtered fluid I add a quarter of an ounce of saccharine matter dissolved in equal parts (say, about half a pint of each) of spirit and water; I prefer grape-sugar so dissolved if the solution is allowed to stand a few hours. The invention is applicable for the manufacture of looking-glasses and every other description of glass, either hollow or with a flat surface, that it is desirable to coat with silver. There is nothing at all unhealthy or injurious in the method thus employed, and no smell of any kind arises from it either during the process or after the glass is silvered. It can be employed either in a horizontal or vertical position, provided the liquid be kept in contact with the surface of the glass intended to be silvered, the glass being kept heated to about 160° F. during the process. As soon as the silver on the glass is perfectly dry it may be varnished with common mastic varnish, which preserves it thoroughly from friction.

"The superiority of this invention over all others yet known consists in its perfect durability, and its withstanding heat to a very extraordinary extent, as well as damp, which renders it equally serviceable in all climates. This solution will deposit silver upon metals in a very perfect manner."

This new method also appears not to have given satisfactory results, for patents were subsequently taken out protecting the use of various reducing agents; these, however, introduced no new principle, nor were they real improvements upon Drayton's procedure.

Among others, in 1855, Hill (Specification, A.D. 1855, 1093) protected a process for silvering glass in which invert sugar was used as the reducing agent (he recommends a temperature of 212° F. for the deposition); later in the same year, Petitjean took out a patent (Specification, A.D. 1855, 1681) in which tartaric acid was employed at a temperature of 150° F.

It must not be overlooked that the difficulties originally met with in manufacturing silver-coated mirrors on a large scale were not entirely due to defects in the silvering process, but also to defects in the glass used or in its polishing and subsequent treatment. It was only after many failures that mirror makers sufficiently recognised what apparently trifling details materially affected the results. For example, if plates of glass after polishing are allowed to remain in a case for some days during transit, separated by strips of paper or flannel, the places where the paper or flannel comes into contact with the glass are clearly distinguishable after silvering, the metal being noticeably duller there than upon the untouched portions.

No really satisfactory method of silvering glass was,

however, devised until Liebig took up the study of the process with the object of finding a liquid able to deposit, at the ordinary temperature, a permanent coherent film of silver which would not later develop spots. Liebig published his results in 1856 (*Annalen*, 1856, xcviii., 132). An important point of his work is that he was the first to notice and employ the effect of caustic alkali in accelerating the rate of reduction of silver. He recommended that the glass should be silvered face downwards in an ammonical solution of silver nitrate containing caustic soda mixed with an aqueous solution of milk-sugar.

To prepare Liebig's silvering solution, 1 grm. of silver nitrate is dissolved in 20 cc. of water, and just enough of a solution of ammonia added to dissolve the silver oxide at first thrown down. This liquid is mixed with 45 cc. of a solution of caustic soda of specific gravity 1·035, and the precipitate again produced, re-dissolved by more ammonia. To ensure the absence of any excess of the latter, which retards the reduction, enough of a dilute solution of silver nitrate is dropped in to produce a slight permanent precipitate. This solution is finally made up with water to 150 cc., and allowed to settle. Immediately before use the clear silvering solution is mixed with one-sixth of its volume of a 10 per cent aqueous solution of milk-sugar. The plate to be silvered is suspended with the face to be coated downwards, so that the glass surface everywhere touches the liquid, and is at least 1 cm. from the bottom of the vessel.

Reduction begins immediately the milk-sugar is added, and is ended in about a quarter of an hour at the ordinary temperature. If the solution is warmed, reduction is much more rapid, and is complete in a few minutes. After washing with distilled water and drying in a warm place, the silver adheres firmly to the glass, and with care can be polished to a perfect mirror. Liebig states than an estimation of the silver thus thrown down showed that 1 square metre of the film produced contained 2·21 grms. of silver.

Much later, Liebig recommended a somewhat different procedure (*Annalen*, 1867, Suppl. V., 257). The silver solution employed is prepared by adding caustic soda to an aqueous solution of silver nitrate containing ammonium sulphate. The reducing liquid is made by mixing two liquids, one a solution of cane-sugar inverted by boiling with tartaric acid, the other a solution of cupric tartrate in caustic soda. Liebig states that he is unable to explain the action of the copper, but that when it is used the silver is much more uniformly deposited and less liable to contain flecks and holes.

Either of Liebig's processes if properly carried out gives a perfectly satisfactory result, and his original process is still preferred by some persons.

Concave mirrors made by depositing silver on a polished glass surface received early an important application in reflecting telescopes. The mirrors used in such instruments were originally constructed of a hard white alloy of copper and tin containing a little arsenic known as speculum metal. Such mirrors had so many grave disadvantages that they have fallen out of general use. The alloy is extremely brittle, and thus liable to fracture, even a sudden change of temperature sometimes causing this; its great weight makes it difficult to mount, and it reflects about one-third less light than silver. Its greatest drawback, however, is its liability to tarnish, after which the mirror can only be again made fit for use by re-polishing and consequently re-figuring, which costs nearly as much as a new one.

The suggestion to use silvered glass in place of speculum metal was originally made by Foucault (*Comptes Rendus*, 1857, xliv., 339), who, apparently unaware of Liebig's recent work, employed films deposited by Drayton's method.

Draper employed such a silvered speculum in his large reflecting telescope, and describes in detail how he silvered it ("Smithsonian Contributions to Knowledge," 1865, xiv.). He, following Foucault, at first used Drayton's process, but like other observers, finding it to give mirrors liable to spot, abandoned it in favour of a modification of one patented by Cimeg in 1861 (Specification, A.D. 1861, No. 619), in which Rochelle salt is used as the reducing agent. Draper states that the thickness of the silver thus deposited is about one two-hundred thousandth of an inch, and that the metal deposited on a circular mirror 15¼ inches in diameter weighs less than 4 grains.

The advantages of reflectors of silvered glass are well seen in Commons' 36-inch Newtonian telescope finished in 1879, and transferred in 1895 to the Lick Observatory, and in the 5-foot reflector constructed by him on a similar plan for the Harvard College Observatory in 1904.

Browning in his book ("A Plea for Reflectors," Sixth Edition, 1876), recommends Liebig's original process for silvering specula, and gives the following very full directions for carrying it out:—"Prepare three standard solutions: (A) Silver nitrate 90 grains dissolved in 4 ozs. of distilled water; (B) caustic potash (purified by dissolving in alcohol) 1 oz., dissolved in 25 ozs. of distilled water; (C) milk sugar in powder 4 oz., dissolved in 5 ozs. of distilled water. Of these solutions, A and B may be kept in stoppered bottles for any length of time, but C must be fresh. To prepare sufficient of the silvering fluid to coat an 8-inch speculum, pour 2 ozs. of Solution A into a glass vessel capable of holding 35 fluid ozs., drop in cautiously, stirring all the time with a glass rod, as much liquid ammonia as is just necessary to obtain a clear solution of the precipitate first thrown down, and add 4 ozs. of Solution B. The brownish black precipitate formed must be just re-dissolved by the addition of more ammonia as before. Dilute the liquid with distilled water until its bulk reaches 15 ozs., and drop in some of Solution A until a slight precipitate, which does not dissolve after stirring for three minutes, is obtained. Then dilute with 15 ozs. more of distilled water, and set the whole aside to settle. Do not filter. When all is ready for immersing the mirror add to this silvering solution 2 ozs. of Solution C, and stir gently and thoroughly. Solution C may, if necessary, be filtered."

(To be continued).

THE

EFFECT OF PRESSURE UPON ARC SPECTRA.*

No. I.—Iron.

By W. GEOFFREY DUFFIELD, B.Sc., B.A.

The first part of the paper contains a description of the mounting and adjustment of the large Rowland Concave Grating in the Physical Laboratory of the Manchester University. The feature of this is the stability of the carriages carrying the grating and camera, and the novel construction and attachment of the cross-beam, which secure the absence of any disturbance which might be caused by bending or sagging.

The second part describes experiments made with a pressure cylinder designed by Mr. J. E. Petavel, F.R.S., in which an arc is formed between metal poles opposite a glass window, through which the light is examined by means of the Grating Spectroscope. A system of mirrors allows the image of the arc, however unsteady it may be, to be kept almost continuously in focus upon the slit.

Two sets of photographs of the iron arc in air have been taken for pressures ranging from 1 to 101 atmospheres (absolute), and the results are given below for wave-lengths $\lambda = 4000$ A.U. to $\lambda = 4500$ A.U.

I. *Broadening.*

1. With increase of pressure all lines become broader.
2. The amount of broadening is different for different

* Abstract of a Paper received by the Royal Society, July 4, 1907.

lines, some almost becoming bands at high pressures, and others remaining comparatively sharp.

3. The broadening may be symmetrical or unsymmetrical; in the latter case the broadening is greater on the red side.

II. *Displacement.*

1. Under pressure the most intense portion of every line is displaced from the position it occupies at a pressure of 1 atmosphere.

2. Reversed as well as bright lines are displaced.

3. With increase of pressure the displacement is towards the red side of the spectrum.

4. The displacement is real and is not due to unsymmetrical broading.

5. The displacements are different for different lines.

6. The lines of the iron arc can be grouped into series according to the amounts of their displacements.

7. Three groups can in this way be distinguished from one another; the displacements of Groups I., II., III. bear to one another the approximate ratio 1 : 2 : 4. (The existence of a Fourth Group is suggested by the behaviour of two lines, but further evidence is needed upon this point; 1 : 2 : 4 : 8 would be the approximate relations existing between the four Groups).

8. Though all the lines examined, with two possible exceptions, fall into one or other of these Groups, the lines belonging to any one Group differ to an appreciable extent among themselves in the amounts of their displacements.

9. The relation between the pressure and the displacement is, in general, a linear one, but some photographs taken at 15, 20, and 25 atmospheres pressure give readings incompatible with this relation, Other photographs at 15 and 25 atmospheres present values which are compatible with it.

10. The abnormal readings are approximately twice those required by the displacements at other pressures, if the displacement is to be a continuous and linear function of the pressure throughout.

11. On the photographs showing abnormal displacements the reversals are more numerous and broader than they are on plates giving normal values, and there is some evidence in favour of a connection between the occurrence of abnormal displacements and the tendency of the lines to reverse.

III. *Reversal.*

1. As the pressure is increased, reversals at first become more numerous and broader.

2. The tendency of the lines to reverse reaches a maximum in the neighbourhood of 20 to 25 atmospheres, and a further increase in pressure reduces their number and width.

3. Two types of reversal appear on the photographs, symmetrical and unsymmetrical.

4. Within the range of pressure investigated, the reversals show no tendency to change their type.

5. In the case of unsymmetrically reversed lines in the electric arc, the reversed portion does not, in general, correspond to the most intense part of the emission line, being usually on its more refrangible side.

6. The displacements of the reversed parts of the unsymmetrically reversed lines of Group III. are about one-half the displacements of the corresponding emission lines. Indeed, the reversed parts of the lines of Group III. fall approximately in Group II.

7. No relation between the order of reversal and the frequency of vibration, such as exists in the spark, has been observed in the iron arc for the ranges of wave-length and pressure examined.

IV. *Intensity.*

1. The intensity of the light emitted by the iron arc is, under high pressures, much greater than at normal atmospheric pressure.

2. Changes in relative intensity of the lines are produced by pressure. Lists of enhanced and weakened lines are given.

THE TITRATION OF MERCUROUS SALTS WITH POTASSIUM PERMANGANATE.

By D. L. RANDALL.

If a solution of a mercurous salt, such as mercurous sulphate in dilute sulphuric acid, is titrated with potassium permanganate in the usual manner, the bleaching of the colour is rapid at first, but long before the oxidation is complete the solution assumes a golden-yellow colour, and on standing the brown oxides of manganese are precipitated. For this reason no definite end-reaction is obtainable. This difficulty is, however, avoided if the permanganate solution is added in excess, the colour then bleached with a standard ferrous sulphate solution, and the end-point finally reached by a few drops of permanganate. Under these conditions the end-reaction is perfectly sharp and the oxidation of the mercurous salt complete, as may be proved by adding hydrochloric acid to the solution.

In the preliminary experiments this process was tested upon weighed portions of commercial chemically pure mercurous sulphate, which was dissolved in dilute sulphuric acid. So much difficulty was experienced in dissolving the salt in quantities suitable for experiment that recourse was taken to the very doubtful procedure of heating the liquid (boiling or prolonged heating on the steam-bath) to hasten the solution. Although the end-reaction was in every case as sharp as could be desired, and the oxidation complete, the results were low and variable, indicating from 90 to 93 per cent of mercurous sulphate in the sample used. This was probably due to the partial oxidation of the mercurous salt during the process of solution.

A few experiments in which the salt was dissolved in hot concentrated phosphoric acid, and the solution then diluted and titrated without further addition of acid, gave results much nearer the theory but still very variable.

For the final experiments a large quantity of a mercurous sulphate solution was prepared by shaking up an excess of the salt in water acidified with sulphuric acid, allowing the whole to stand for twenty-four hours, and finally filtering through asbestos. Portions of this solution for standardisation or titration were measured out in a 100 cc. burette or weighed out in a dry counterpoised beaker. The standard of this solution was obtained by precipitating the measured or weighed portions in the cold with a slight excess of sodium chloride. After twelve hours' standing, the precipitated mercurous chloride was collected upon asbestos in a platinum crucible and dried to a constant weight at the ordinary temperature in a vacuum desiccator over sulphuric acid. The method of drying in a vacuum is recommended by Hulett (*Zeit. Phys. Chem.*, 1904, xlix., 500) as much more trustworthy than the usual one of drying in the air-bath at 105—110° C., where there is danger of volatilisation—a statement which the experience of the present writer has fully borne out. (Hulett, however, employed calcium chloride instead of sulphuric acid as the drying agent; Treadwell, *Lehrbuch Anal. Chemie*, ii., 114, states that when the drying is carried out at 105° the results are always about 0·4 per cent too low). In every case the standard of the mercurous solution used was fixed by two or more gravimetric determinations made on the same day as the corresponding series of titrations.

The solutions of permanganate and of ferrous sulphate used were both approximately twentieth normal. The reason why it is desirable to use solutions more dilute than the usual tenth normal strength is obvious when we note that 0·1 cc. of the above twentieth normal permanganate is equivalent to about 1 mgrm. of mercury. For the same reason the titrations must be performed with all possible care and accuracy. All the burettes used in the present investigation had been standardised by the Berlin Reichsanstalt.

As the oxidation of mercurous salt by an excess of permanganate is very rapid, no great care is necessary in regulating the amount of the excess. It is sufficient in

Table I.

Hg_2SO_4 solution.	Dilution at titration.	H_2SO_4 (1 : 1)	$KMnO_4$ approx. N/20	$FeSO_4 = KMnO_4$.		$KMnO_4$ final.	Hg found	Hg theory	Error
Cc.	Cc.	Cc.	Cc.	Cc.	Cc	Cc.	Grm.	Grm.	Grm.
				A.					
100	150	5	14·70	10	10·90	3·80	0·0340	0·0354	− 0·0008
100	150	5	14·72	10	10·90	3·82	0·0347	0·0354	− 0·0007
100	150	5	14·70	10	10·90	3·80	0·0340	0·0354	− 0·0008
100	150	5	14·71	10	10·90	3·81	0·0346	0·0354	− 0·0008
				B.					
Grms.									
505·8	500	5	29·20	10	10·90	18·30	0·1668	0·1666	+ 0·0002
500·2	500	5	32·16	13	14·17	17·99	0·1639	0·1648	− 0·0009
510·1	500	5	29·29	10	10·90	18·39	0·1676	0·1680	− 0·0004
499·2	500	5	28·95	10	10·90	18·05	0·1643	0·1644	+ 0·0001

Table II.

$FeSO_4$.	Dilution.	H_2SO_4 (1 : 1).	HNO_3.	Approx. N/10 $KMnO_4$.
Cc.	Cc.	Cc.	Cc.	Cc.
25	200	5	0	13·37
25	200	5	0	13·39
25	200	5	0	13·41
25	200	5	0	13·38
25	200	5	0	13·38
25	200	0	3	13·38
25	200	0	5	13·40
25	200	0	5	13·41
25	200	0	5	13·40
25	200	0	5	13·38
25 (*a*)	200	5	0	13·47
25	200	5	0	13·50
25	200	5	0	13·49
25	200	0	5	13·53
25	200	0	10	13·50
25	200	0	20	13·51
20	200	0	30	13·00

(*a*) Changed $FeSO_4$ solution.

Table III.

$Hg_2(NO_3)_2$ solution.	Dilution.	HNO_3.	Approx. N/20 $KMnO_4$.	$FeSO_4 = KMnO_4$.		$KMnO_4$ final. = Hg found.	Hg theory.	Error.
Cc.	Cc.	Cc.	Cc.	Cc.	Cc.	Cc.	Grm.	Grm.	Grm.
25	200	5	49·99	9·76	10·64	39·35	0·3586	0·3594	− 0·0008
25	200	5	49·68	9·50	10·36	39·32	0·3583	0·3594	− 0·0011
25	200	5	49·73	9·50	10·36	39·37	0·3588	0·3594	− 0·0006
25	200	5	49·89	9·67	10·54	39·35	0·3586	0·3594	− 0·0008
25	200	5	49·70	9·50	10·36	39·34	0·3585	0·3594	− 0·0009
		H_2SO_4 (1 : 1).							
25	200	5	50·29	10·00	10·90	39·39	0·3589	0·3594	− 0·0005

practice to continue the addition of permanganate until the solution, coloured brown by the oxides of manganese, takes on a distinctly red tint. Under these circumstances the ferrous sulphate can be added immediately, and the titration completed. Table I. gives the results obtained with mercurous sulphate.

For practical purposes the application of the method to mercurous nitrate is of much greater importance. In Schneider's method for the determination of manganese (*Ding. Pol. Journ.*, cclxix., 224), permanganic acid is titrated with hydrogen peroxide in the presence of nitric acid. Ibbotson and Brearley (Chemical News, lxxxiv., 247) in their modification of this process recommend the use of standard ferrous ammonium sulphate instead of hydrogen peroxide. Blair also studied this process, and recommends the use of ferrous ammonium sulphate (*Journ. Am. Chem. Soc.*, xxvi., 793; also "Chemical Analysis of Iron," Sixth Edition, p. 121). In the absence of any data concerning the quantity of nitric acid that can safely be present in the titrations of ferrous sulphate the determinations in Table II. were made. The nitric acid used was rendered free from the lower oxides of nitrogen by the prolonged passage of a current of air. The acid used in all the subsequent experiments was purified in a similar manner.

When more than 10 per cent by volume (20 cc. in 200 cc.) of the concentrated acid was present, the oxidation of the ferrous salt by the nitric acid was evident in the change of colour of the solution, low results, and uncertain end reaction.

(Note.—As nitrous acid is at least in part oxidised by direct titration with potassium permanganate, and completely when an excess is used—method of Kinnecut and Nef, *Am. Chem. Journ.*, v., 388—only a part of the loss due to oxidation of the ferrous salt by the nitrous acid would appear in the result).

This table shows that when the titration is made without unnecessary delay after adding the acid, as was the case here, 3 per cent of pure nitric acid, the amount used in the subsequent experiments, has no appreciable effect on the estimation of ferrous iron.

In Table III. are given the results of a series of determinations of mercurous nitrate by the method described above. A solution was prepared by dissolving the crystallised salt in water containing enough pure nitric acid to prevent the formation of basic salts. As an additional precaution a current of hydrogen, washed by alkaline permanganate and alkaline pyrogallol, was passed for twelve hours through the solution to remove nitrous acid. Measured portions of this solution, which was standardised

gravimetrically as given above, were diluted to 200 cc., further acidified with pure nitric acid, and titrated in the manner already described.

In the last experiment sulphuric acid was added instead of nitric acid, yet, as the table indicates, without apparent effect on the result.

This investigation has shown :—

1. That mercurous sulphate and mercurous nitrate can be readily estimated by potassium permanganate with a very fair degree of accuracy.

2. That ferrous salts can be successfully titrated in the presence of at least 3 per cent of nitric acid.

In closing, the writer gratefully acknowledges the suggestions of Dr. R. G. Van Name which led to this investigation.—*American Journal of Science*, xxiii., p. 137.

A REVISION OF THE ATOMIC WEIGHT OF POTASSIUM.*

II. The Analysis of Potassic Bromide.

By THEODORE WM. RICHARDS and EDWARD MUELLER.

Introduction.

The foregoing quantitative study of potassic chloride by Dr. Arthur Staehler and one of the present authors affords strong evidence that the atomic weight of potassium is about 39·114, slightly lower than the value based upon the work of Stas. The authors fully appreciated, however, that the investigation of a single compound is not enough to establish a chemical constant so important as this, and, accordingly, the present investigation was prosecuted simultaneously. It was expected that the two investigations might either support one another, or else, by affording incompatible results, lead to the discovery of a constant error in one or the other, and thus pave the way for further advance in knowledge. As will be seen, the work on the chloride was satisfactorily confirmed by the work on the bromide.

In the present case the careful study of potassic bromide was particularly necessary, because there already exist two concordant series of experiments upon this substance, performed by the old masters, Marignac and Stas, pointing to a value in the neighbourhood of 39·14, instead of the before-mentioned new value 39·11. In this case the higher value for potassium is not diminished, as in the case of the chloride, by an additive correction in the atomic weight of the halogen, because Baxter has shown Stas's estimate for bromine to have been nearly correct. Hence, the discrepancy remains one too serious to be tolerated.

(A brief review of Stas's and Marignac's work may be found in Clarke's "Re-calculations," 1897, p. 47. Baxter's work is to be found in *Proc. Am. Acad.*, 1906, xlii., 201 ; *Journ. Am. Chem. Soc.*, 1906, xxviii., 1322. See also Richards, *Trans. Am. Phil. Soc.*, 1904, xliii., 116).

The careful study of this work of Stas and Marignac affords convincing evidence that the potassic bromide used by them for analysis was not sufficiently pure for the purpose. Stas admitted that some of his preparations were not even wholly soluble in water, and his method of procedure was such that some of them probably contained platinum and hydroxide. Because speculations of this kind concerning work so long past are of but little value, it was clearly necessary to repeat this work with modern care, and the following pages recount the details of the repetition.

In common with others of the same type, the investigation easily resolves itself into several sections, and will be discussed under the following heads :—The preparation of materials, the drying and weighing of potassic bromide, the determination of the ratio of argentic to potassic bromide ; the determination of the ratio of silver to potassic bromide, and the discussion of the results. Of the laboratory tasks the preparation of the materials was by far the most laborious and puzzling, while the analytical work was comparatively simple.

The Preparation of Materials.

The Source of the Potassium.—The task of preparing pure potassic bromide, simple as it may appear, is by no means an easy one. In view of our experience, it seems probable that neither Marignac nor Stas ever prepared samples pure enough to correspond with the other precautions which they took. As in the case of sodic bromide, the salt itself when once made cannot be effectively purified (Richards and Wells, *Proc. Am. Acad.*, 1906, xli., 435 ; *Zeit. Phys. Chem.*, 1906, lvi., 348). In this respect it differs widely from the chloride. We found after due trial that the potassium and bromine must be purified separately in such forms as to introduce no foreign matter. Accordingly, the two substances, already adequately purified, were caused afterwards to yield potassic bromide ; and this salt, when re-crystallised, gave the final substance for analysis. The purification of the potassium materials will be discussed first.

It was necessary to provide potassium material which should be free from the suspicion of introducing any impurity with the metal desired, either basic or acid. Potassic nitrate, which had served so well in the case of the chloride, was not suitable for the present purpose, because the destruction of the nitric acid involves too great a sacrifice of laboriously prepared hydrobromic acid. After due consideration, potassic oxalate was tentatively chosen. It was necessary to prove that this salt can be easily and certainly purified by re-crystallisation, and especially to show that the other alkali metals can thus be separated. The following tests accomplish this proof :—

A saturated solution of potassic oxalate containing a purposely added admixture of 10 per cent of sodic oxalate was crystallised, and the crystals drained centrifugally. By the flame test, a pronounced difference was noticeable between the amount of sodium present in the mother-liquor and that in the crystals. A second re-crystallisation and whirling was still more satisfactory ; the crystals gave no sodium test to the eye, while the mother-liquors gave a distinct yellow. This indicates that sodium has a decided tendency into the mother-liquors, and hence can be separated by fractional crystallisation.

Again, 1 per cent of lithium salt was added to potassic oxalate with similar outcome. Rubidium and cæsium were tested likewise. A saturated solution of potassic oxalate and a salt of each of these metals was made of such strength that the rubidium or cæsium could easily be found by means of the spectroscope. Each solution was evaporated until saturated, and cooled ; and the crystals were whirled. The mother-liquor gave a test for the impurity, the crystals gave none.

No other oxalates were seriously to be feared, because the insoluble ones would appear at once and demand filtration, and soluble double oxalates could hardly be isomorphous, and would therefore tend into the mother-liquors. Traces of calcic oxalate in fact appeared in the former fashion, and traces of iron in the latter.

In view of these satisfactory results, it was evidently only necessary to crystallise the potassic oxalate often enough to make the separation complete ; and since potassic oxalate has a fairly convenient change in solubility with the temperature, the yield after a considerable number of crystallisations is good, especially if pains are taken to carry out the process systematically.

Two very pure samples of oxalate were made, from two different sources. As one source of material, a commercial sample prepared by Merck was used. It had been labelled "Potassium oxalate, neutral, highest purity," and contained, as a matter of fact, only the traces of calcium and iron already referred to, but no lead or other discoverable impurity. A large quantity of a solution of this salt was filtered hot into a platinum dish, where it was five times systematically re-crystallised, the crystals being centrifugally whirled each time.

* *Publication* No. 69, Carnegie Institution of Washington.

Careful scrutiny in the spectroscope revealed in the product no other spectroscopic lines than those of potassium, and careful qualitative tests proved the absence of lead and iron. The salt dissolved without a trace of residue in water, and was quite pure enough to serve as a starting point for further operations, to be described under the heading "Potassic Bromide."

A second sample of potassic material was obtained from Merck in the form of the hydroxide, being marked "Potassium Hydrate, Chemically pure Reagent; conforms to the standards of Dr. Krauch." It was, in fact, very pure, giving a perfectly clear solution both before and after neutralisation. It was neutralised with a specimen of oxalic acid which had been carefully purified by Mr. G. E. Behr, jun., for other work. This acid contained no halogens, and left no residue on volatilisation in platinum. Slightly more than the equivalent quantity of acid was added, and the oxalate obtained was therefore slightly acid. As will be shown, the acidity was later the cause of much inconvenience, and had better have been avoided. The oxalate was four times systematically re-crystallised in platinum with centrifugal draining each time. The final product, like the previous one, gave no tests for impurities except a slight excess of acid; it was used as the source of potassium for one preparation of potassium bromide.

Bromine.—Although the methods previously used at Harvard had afforded a satisfactory yield of very pure bromine, it was desired to add to the knowledge on the subject by testing another method (see *Proc. Am. Phil. Soc.*, 1904, xliii., 119; for references, and Stas, *Mém. Acad. Belgique*, 1882, xliii., II., 38). Through the generosity of the Mallinckrodt Chemical Works of St. Louis, Missouri, and also of the Dow Chemical Works of Midland, Michigan, a large quantity of potassic bromate was placed at our disposal. Repeated crystallisation, very kindly carried out for us on a large scale by these firms, had been the method used in its purification.

This material, which served as our starting-point, was already very pure, a fact which was indicated by three syntheses of argentic bromide from purest silver and potassic bromide obtained by decomposing the Mallinckrodt bromate. These syntheses, carried out with all necessary precautions, gave, respectively, 57·441, 57·440, 57·441 as the percentage of silver in argentic bromide. According to Baxter the true amount is 57·445 (Baxter, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1332; see also Richards, *Trans. Am. Phil. Soc.*, 1904, xliii., 119). The slight difference indicates a trace of iodine rather than chlorine; but this impurity can be easily expelled, while chlorine is far more troublesome.

It having been demonstrated that re-crystallisation is an effective means of purifying the salt from chlorate and chloride, a large quantity of potassic bromate was three times re-crystallised in porcelain, the crystals being centrifugally whirled each time and all mother-liquors discarded. This gave an exceedingly pure bromate, much purer than Stas could have obtained ("Untersuchungen," 160), because the centrifugal draining makes so great a difference in the rate of purification (Richards, *Journ. Am. Chem. Soc.*, 1905, xxvii., 104).

A large quantity of the salt was decomposed into the bromide in a platinum dish by the heat of an alcohol lamp. The potassic bromate in decomposing attacked the platinum, and the mass of bromide was slightly brownish in colour, but this caused no inconvenience in the present case, as the bromine was to be subsequently distilled. In order to liberate the halogen, the bromide was treated in strong solution with less than the calculated quantity of bromate and an excess of pure sulphuric acid. The acid was added drop by drop to the mixed solution of salts in an apparatus made entirely of Jena glass, which was kept surrounded by ice-water. The bromine which volatilised on account of the heat of the reaction was caught in a condenser under water; to this was added the remaining bromine, which had been separated from the supernatant solution by means of a separating funnel.

The bromine thus obtained was twice distilled by steam heat into water in a Jena glass condenser, packed in ice. It was kept in a well-seasoned bottle with double ground-glass stoppers.

The product was certainly free from non-volatile materials, and could have contained only iodine, and, perhaps, a trace of sulphuric acid as impurity. It will be seen that these were eliminated in the subsequent work. This was the only sample of bromine prepared; it was used in all the preparations of bromide, as the quantitative results indicated that it was very pure.

Potassic Bromide.—The problem of obtaining potassic bromide from the oxalate and bromine had been carefully considered before these substances had been prepared. Only two methods recommended themselves for the present purpose, although the bromide can be obtained from these two materials by a variety of reactions, which would ordinarily be acceptable. Here, however, simplicity, completeness, and theoretical correctness must all be fulfilled; that the methods adopted really possessed these advantages in their favour must be admitted after careful perusal of the following description of the details.

In some preliminary experiments it was shown that by adding an excess of bromine to the oxalate and evaporating off the excess, a very pure bromide quite free from oxalate is obtained. Accordingly, a quantity of the first sample of five times crystallised potassic oxalate was treated with an excess of bromine, the bromine being added in small quantities from a dropping-funnel. The solution was held in a quartz dish, which was carefully hooded to prevent entrance of dust. When the action had ceased, the solution was heated on a steam-bath until any traces of iodine and all excess of bromine had been expelled. The solution was found to be entirely free from oxalic acid upon testing with calcic nitrate in a solution faintly acid with nitric acid. Although it was wholly colourless while in the quartz dish, after being concentrated in platinum it developed a very faint yellow tinge. Upon re-crystallising three times this colour was finally concentrated in the extreme mother-liquor, and was found to be due to a trace of platinum; no iron was present. Even the first crystals were perfectly white, the second and third mother-liquors also showed no trace of colour, and only the first of the mother-liquors gave a test for platinum.

The material thus prepared, after being three times re-crystallised in platinum with centrifugal draining, was called Sample I., and served for Analyses 1 to 11.

The second sample of potassic bromide was prepared from the second sample of four times re-crystallised potassic oxalate. The method was the same as with the previous sample. An excess of bromine was added to the oxalate in quartz; when action ceased, the bromine was driven off by heating on steam-bath. However, on testing for oxalate, a perceptible quantity was found still undecomposed. This was unexpected, in view of the fact that the first preparation of bromide had given no trouble in this respect. The difficulty was traced to the presence of a small percentage of acid salt in the oxalate; the presence of acid has an inhibitory effect on the reaction of bromine on the oxalate ion. Obviously, the simplest remedy would have been to add pure potassic hydroxide; but this was not added because at that moment there was none at hand. Moreover, because the reaction was being performed in quartz, it was thought best not to use a caustic alkali for fear that the dish might be slightly attacked. The addition of a small amount of very pure re-crystallised bromate to this slightly acid solution served better, because its use was unattended with danger. Its employment was entirely effective; the ionised hydrogen was removed, and after adding more bromine and heating, a solution of bromide was obtained which contained no trace of oxalate.

This specimen was re-crystallised entirely in quartz, in order to prevent a recurrence of the trouble experienced with Sample I., as well as to see if the variation of conditions, affected the atomic weight. Two crystallisations

were made with centrifugal draining, and every precaution; and there was obtained finally a very pure colourless product, with which were made two analyses, Nos. 12 and 13. That a uniformly pure material had been made is shown by the close agreement of these two analyses with the mean of all.

As a further precaution against accidental error, it was thought best to develope a method essentially different from that just discussed, and to prepare therewith a third specimen of bromide. In brief, this method consisted in the separate preparation of pure ammonic bromide and potassic hydroxide, and the production of potassic bromide by the evaporation of the mixed solutions of these substances. Thus can be obtained a salt contaminated only with excess of volatile ammonic bromide.

The preparation of pure ammonic bromide was very easy. Ammonia essentially free from carbon compounds was redistilled into water in a platinum dish. Into this was dropped the purest bromine, which fell through the liquid into a small porcelain crucible resting on the bottom of the dish. In this way the bromine itself could not come into contact with platinum and attack it. The reaction took place very rapidly, yielding ammonic bromide which could have contained no non-volatile ingredients, because all its constituents had just been distilled.

The preparation of pure potassic hydroxide was less easy to devise, because more original; but the execution was almost as easy. The problem was solved by the use of an electrolytic process which will be described in greater detail elsewhere. In brief, a saturated solution of potassic oxalate (Sample I.) was electrolysed between a pure mercury cathode and a platinum anode in a porcelain dish cooled with ice, the current from four storage cells being used. When the amalgam became solid, the current was stopped, the solution decanted, and the amalgam washed, being triturated with an agate pestle under water, till no test for oxalate could be obtained. The pure amalgam was transferred to a platinum dish, covered with water, and made the anode of a dense current until only a little of the potassium amalgam remained undecomposed. Thus pure potassic hydroxide was formed. This solution was poured into the ammonic bromide solution, the mixture was evaporated and crystallised, and the salt thus obtained used for Analyses 14, 15, and 16.

The bromide thus obtained must have been very pure. During the electrolysis, the high concentration of the potassic oxalate (see Bunge, *Berichte*, 1876, ix., 78) would tend to allow the deposition of potassium only (Berthelot, *Ann. Chim. Phys.*, 1879, [5], xviii., 433). At any rate, metals less easy to deionise could hardly have been set free. During the later decomposition of water by the amalgam, all metals with less tendency to ionise would have remained in the mercury, because some of the amalgam was left undecomposed. Any trace of iodine which the bromine may have contained must have been driven off by the fusion just before analysis, this fusion being prolonged in order to expel ammonic bromide. The results of the analyses of this sample indicate its essential identity with the two preceding preparations. Since there was no known source of impurity in any one of the preparations, this was not surprising.

Although our consistent employment of insoluble vessels rendered the presence of colloidal silica unlikely, an effort was made to test for this impurity of sample II. by volatilising 3 grms. of it in a stream of nitrogen. Unfortunately, the high temperature of the electric furnace caused the platinum boat containing the salt to weld to the foil which surrounded it in the tube, so that no certain quantitative evidence could be obtained. Two minute black spots were visible in the boat; nothing else could be seen upon very careful scrutiny. If there were any silica present, the amount must have been too small to have had any appreciable influence on the final atomic weights. Time and material were lacking, hence the experiment was not repeated.

Silver.—The essential details of the preparation of pure silver, as developed by Richards and Wells, were followed in detail, and the reader is referred to their paper, as well as to the preceding paper of Richards and Staehler, for the particulars. Two samples of silver were made; they were found to be identical in quantitative behaviour.

The source of the material used for the first preparation was the pure precipitated argentic chloride remaining from the work of Richards and Wells on sodium. It was reduced to metallic silver with invert sugar in a strong solution of sodic hydroxide. The silver thus obtained was washed free from soluble matter and dissolved in nitric acid; the argentic nitrate after crystallisation and whirling was reduced with ammonic formate, yielding a beautiful crystalline mass of metal.

This pure silver, after very thorough washing, was fused on lime by means of a blast lamp whose tip had been carefully cleaned. The buttons which were thus obtained were cooled in the reducing-flame, washed free from lime, scrubbed with cleaned sea-sand, etched with strong nitric acid, and washed with the purest water, to serve as anodes in the electrolytic purification which was the next step. The electrolysis was carried on as already described in previous similar Harvard researches, and every step of the subsequent work may be found in detail in the preceding papers on sodic and potassic chloride (see *Proc. Am. Acad.*, 1903, xxxviii., 450; Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 473; Richards and Staehler, *Publication* 69, Carnegie Institution of Washington; Chemical News, xcvi., p. 133). The metal was finally fused as usual on a boat of the purest lime in an atmosphere of hydrogen under a tension of 50 mm. The larger pieces, after etching with nitric acid, were cut into smaller ones of convenient size with a clean cold-chisel. They were again etched in order to dissolve all traces of iron, scrubbed with clean sand, washed with a jet of water, and etched yet again with acid, paying particular attention to the cut edges. (Richards and Archibald, *Proc. Amer. Acad.*, 1903, xxxviii., 450; Baxter, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1329). Finally the pieces were dried over an alcohol lamp and kept in a desiccator over potassic hydroxide for use.

This silver was used both in most of the titrations against potassic bromide and as the source of argentic nitrate used in the precipitation of argentic bromide to be weighed.

A second sample of silver, prepared from somewhat less pure initial material, was put through a more elaborate and exhaustive round of purification, which need not be detailed. The preparation included five crystallisations as nitrate and two successive precipitations as metal by formate. This silver was fused into buttons of a size suitable for immediate use without cutting. They were cleaned by etching and washing, dried, and preserved free from impurity as usual, and were used in analyses 7 and 9.

Nitric Acid.—For preliminary work, ordinary "chemically pure" nitric acid was distilled once, using a platinum condenser and Jena glass receiver, the first third of the acid being discarded. For the final analyses this re-distilled product, already very pure, was once again distilled, as before, the first third being rejected. This distillate gave no test with the nephelometer, after dilution.

Water.—As usual in such work, all the water used had been carefully purified by double distillation, once from a fairly strong solution of alkaline potassic permanganate, and then alone. The distillate was caught in Jena glass receiving flasks, which were provided with special adapters to prevent the access of dust. The first and last fractions were always rejected, only the middle portion being used. The connection of the Jena glass boiling-flask with the pure tin condenser was made without rubber or cork (Richards, *Proc. Amer. Acad.*, 1894, xxx., 380). Such water gave every evidence of sufficient purity, as has been frequently pointed out.

The Laboratory.—A very essential precaution in every stage of this work was to effectually exclude hydrochloric acid. Accordingly, all the preparations of the bromide

were carried out in a private laboratory, used especially and only for this work, and wholly free from the interference caused by large classes or other researches. Great care was taken not to allow any hydrochloric acid in the room; indeed, not a drop was used there during the entire research. A separate ventilating fan prevented fumes from other laboratories from interfering with the work.

Utensils.—As usual, great care was taken to avoid the use of any vessels which under the given conditions might be attacked and thus pollute the substance in hand. When glass and porcelain were not harmful, as in the early stages of the preparation of silver, such receptacles were employed; but in the purification of the substance for analysis, platinum and quartz were always used.

(To be continued).

THE

APPLICATIONS OF GRIGNARD'S REACTION.*

By ALEX. McKENZIE, M.A., D.Sc., Ph.D.

(Continued from p. 145).

Section I. (*continued*).

Hydrocarbons.

(*a*) *Unsaturated Hydrocarbons.*—When the Grignard reaction is applied to aldehydes, ketones, &c., sometimes an unsaturated hydrocarbon is obtained instead of an alcohol. It is, in fact, often possible to select the experimental conditions so that either an alcohol or the unsaturated hydrocarbon, obtained from it by the elimination of water, is the product of the action; for example, Grignard obtains phenyldimethylcarbinol, $C_6H_5.C(OH)(CH_3)_2$, from magnesium methyl iodide (1 mol.) and acetophenone (1 mol.) (*Comptes Rendus*, 1900, cxxx., 1322; compare W. H. Perkin, jun., and Pickles, *Trans. Chem. Soc.*, 1905, lxxxvii., 671). If, however, magnesium methyl iodide (2 mols.) is added to acetophenone (1 mol.), the ether expelled, and the residue heated for six hours at 100°, the unsaturated hydrocarbon, metho-(1')-vinylbenzene, $C_6H_5{>}C{:}CH_2$, results (Klages, *Ber.*, 1902, xxxv., 2633). Similarly, it is possible to prepare from mesityl oxide, $CH_3{>}C{:}CH.CO.CH_3$, either the hydrocarbon, $CH_3{>}C{:}CH.C{\lessdot}^{CH_3}_{CH_2}$ (Grignard, *Comptes Rendus*, 1900, cxxx., 1324), or the alcohol, $CH_3{>}C{:}CH.C(OH)(CH_3)_2$ (Fellenberg, *Ber.*, 1904, xxxvii., 3578). To quote a third example, Kay and Perkin (*Trans. Chem. Soc.*, 1906, lxxxix., 839; compare also *Ibid.*, 1905, lxxxvii., 1100), starting with optically active ethyl Δ^1-tetrahydro-*p*-toluate, $CH_3.CH{<}^{CH_2.CH}_{CH_2.CH_2}{>}C.COOC_2H_5$, obtain, by the action of magnesium methyl iodide, optically active Δ^8-*p*-menthenol (8), $CH_3.CH{<}^{CH_2.CH}_{CH_2.CH_2}{>}C.C(OH)(CH_3)_2$. When the latter compound, however, is simply left in contact with an ethereal solution of magnesium methyl iodide at the ordinary temperature, it is converted into the corresponding optically active unsaturated hydrocarbon, $\Delta^{3.8(9)}$-*p*-menthadiene, $CH_3.CH{<}^{CH_2.CH}_{CH_2.CH_2}{>}C.C{\lessdot}^{CH_3}_{CH_2}$.

In many cases only unsaturated hydrocarbons can be obtained, and not the corresponding tertiary alcohols, if it so happens that the latter are very unstable. Klages, in particular, prepared a large number of unsaturated 1'-alkylated styrenes, of which an example has already been quoted, namely, metho-(1')-vinylbenzene. When this hydrocarbon is reduced, it is converted into *iso*propylbenzene, $C_6H_5.CH(CH_3)_2$, with great ease. This method in the hands of Klages has proved highly useful for making a large number of saturated benzenoid hydrocarbons, which are difficult to prepare by other methods.

Various stilbene derivatives have been studied by F. and L. Sachs (*Ber.*, 1905, xxxviii., 511). Thus, *p*-dimethyl aminobenzaldehyde, $(CH_3)_2N.C_6H_4.CHO$, with magnesium benzyl chloride gives the alcohol—

$$(CH_3)_2N.C_6H_4.CH(OH).CH_2C_6H_5,$$

and this, on distillation under diminished pressure, forms 4-dimethylaminostilbene, $(CH_3)_2N.C_6H_4.CH{:}CHC_6H_5$.

The same authors (*Ber.*, 1905, xxxviii., 517; compare Sachs and Michaelis, *Ber.*, 1906, xxxix., 2163) acted on *p*-dimethylaminobenzaldehyde with magnesium methyl iodide, and obtained methyl *p*-dimethylaminophenylcarbinol, $(CH_3)_2N.C_6H_4.CH(OH).CH_3$, from which, however, water was not eliminated in the manner expected. Klages's method of heating the reaction product with an excess of magnesium alkyl halide at 100° did not lead to the formation of dimethylaminostyrene as was anticipated, but N-dimethylcumidine was formed thus:—

$$(CH_3)_2N.C_6H_4.CH(OMgBr).CH_3 + CH_3MgBr = = (CH_3)_2N.C_6H_4.CH(CH_3)_2 + MgO + MgBr_2.$$

The formation of hydrocarbons of the acetylene series by aid of the Grignard action has been imperfectly studied. According to Oddo (*Atti R. Accad. Lincei*, 1904, [5], xiii., 187), magnesium bromoacetylene, CH CMgBr, is produced when a current of dry acetylene is passed into magnesium phenyl bromide, and from this derivatives of the acetylene series are obtained.

(*b*) *Saturated Hydrocarbons.*—Magnesium organic compounds are vigorously acted on by water with the production of hydrocarbons. This was one of the first observations which Grignard made with his reagents (*Ann. Chim. Phys.*, 1901, xxiv., 438; Tissier and Grignard, *Comptes Rendus*, 1901, cxxxii., 835). Methane, for example, is evolved by the addition of water to magnesium methyl iodide: $CH_3MgI + H_2O = CH_4 + MgIOH$.

An alcohol has the same effect as water. For example, $CH_3MgI + C_2H_5OH = CH_4 + OC_2H_5.MgI$.

Indeed, any compound containing a hydroxyl group behaves in this manner, this property of hydroxylic compounds having been recommended both as a means for their qualitative detection and for separating them from compounds which do not interact with the Grignard reagent (Tschugaeff, *Ber.*, 1902, xxxv., 3912). A method for the estimation of hydroxyl groups in carbon compounds is based by Hibbert and Sudborough on this reaction, where, however, amyl ether is substituted for ethyl ether in the preparation of the reagent (*Trans. Chem. Soc.*, 1904, lxxxv., 933). Zerewitinoff claims the method to be suitable for estimating the number of hydroxyl groups in a carbon compound (*Ber.*, 1907, xl., 2023).

Allotropic compounds generally act on the Grignard reagent in accordance with the hydroxylic structure; thus *l*-menthylacetoacetate reacts in accordance with the formula $CH_3.C(OH){:}CH.COOC_{10}H_{19}$, and not as $CH_3.CO.CH_2.COOC_{10}H_{19}$ (McKenzie, *Trans. Chem. Soc.*, 1906, lxxxix., 380).

A regular current of methane is evolved by the addition of dry powdered ammonium chloride to magnesium methyl iodide (Houben, *Ber.*, 1905, xxxviii., 3017): $2CH_3MgI + NH_4Cl = 2CH_4 + NH_2.MgI + MgICl$. When a current of dry ammonia is passed into an ethereal solution of magnesium ethyl iodide, ethane is evolved: $C_2H_5MgI + NH_3 = C_2H_6 + NH_2MgI$. Primary or secondary amines exhibit a similar behaviour. Thus with aniline and methyl aniline:—

$$C_2H_5MgI + C_6H_5.NH_2 = C_2H_6 + C_6H_5.NH.MgI,$$
$$C_2H_5MgI + C_6H_5.NHCH_3 = C_2H_6 + C_6H_5N(CH_3).MgI$$

(Meunier, *Comptes Rendus*, 1903, cxxxvi., 758; *Bull. Soc. Chim.*, 1903, xxix., 314).

The action of a primary amine is possibly, however,

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* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

more complex than this representation of Meunier, since Houben (*Ber.*, 1905, xxxviii., 3017) concludes that the action $2CH_3MgI + C_6H_5NH_2 = C_6H_5NH.MgI,CH_3MgI + CH_4$ takes place in the cold if the proportions of magnesium methyl iodide and aniline, indicated by the equation given, are used (compare Sudborough and Hibbert, *Proc. Chem. Soc.*, 1904, xx., 165). If, however, a second molecular proportion of aniline is added to the hot solution, methane is again evolved, thus :—

$$C_6H_5.NH.MgI,CH_3MgI + C_6H_5NH_2 = 2C_6H_5.NHMgI + CH_4.$$

A method for making aromatic hydrocarbons has been devised by Werner and Zilkens, who use the methyl sulphate (*Ber.*, 1903, xxxvi., 2116, 3618; compare Houben, *Ibid.*, 3083). Thus *p*-xylene in a 75 per cent yield is obtained from magnesium *p*-tolyl bromide :—

$$CH_3.C_6H_4.MgBr + (CH_3)_2SO_4 = C_6H_4(CH_3)_2 + CH_3.SO_4.MgBr.$$

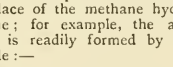
Toluene is obtained from magnesium phenyl bromide in a similar manner.

In order to throw some light on the constitution of triphenylmethyl, Gomberg and Cone (*Ber.*, 1906, xxxix., 1461, 2957) prepared tetraphenylmethane by the interaction of magnesium phenyl bromide and triphenylchloromethane: $C_6H_5MgBr + (C_6H_5)_3CCl = (C_6H_5)_4C + MgClBr$.

The method renders possible the introduction of various radicals in place of the methane hydrogen atom in triphenylmethane; for example, the asymmetrical tetraphenylethane is readily formed by aid of magnesium benzyl chloride :—

$$C_6H_5.CH_2.MgCl + (C_6H_5)_3CCl = (C_6H_5)_3C.CH_2C_6H_5 + MgCl_2.$$

Triphenylchloromethane forms two isomeric magnesium compounds; the α-form possibly has the formula—



and the β-form—

$$(C_6H_5)_3C.MgCl,$$

each one of which appears to interact with triphenylchloromethane to give triphenylmethyl. The bearing of these isomeric compounds on the constitution of triphenylmethyl is at present under discussion (Schmidlin, *Ber.*, 1907, xl., 2316).

Acids.

(*a*) *Carboxylic Acids.*—Grignard was the first to study the action of carbon dioxide on magnesium alkyl halides (*Annales de l'Université de Lyon*, 1901, vi., 1; *Ann. Chim. Phys.*, 1901, [7], xxiv., 435). He found, for example, that when a current of carbon dioxide is passed through an ethereal solution of magnesium methyl iodide, and the product then decomposed by dilute acid, acetic acid is formed :—

$$CH_3MgI + CO_2 = CH_3.COOMgI,$$
$$CH_3.COOMgI + H_2O = CH_3.COOH + MgIOH.$$

This action has been extensively applied, amongst others, by Zelinsky (*Ber.*, 1902, xxxv., 2687, 2692, 4415; 1903, xxxvi., 208), Bodroux (*Bull. Soc. Chim.*, 1904, [3], xxxi., 30), and especially by Houben. It has already been pointed out, however, that, under certain conditions, a carboxylic acid may result from this action either in very small yield or not at all (see section on Tertiary Alcohols). The method, however, in most cases is very successful. Houben gives it as a general one for making aromatic and hydroaromatic carboxylic acids; terephthalic acid, for example, is readily obtained from *p*-dibromobenzene. The yields are often exceedingly good; for example, Schmidlin (*Ber.*, 1906, xxxix., 628) obtains an 83 per cent yield of triphenylacetic acid from triphenylchloromethane.

The action of the Grignard reagent on ethyl chlorocarbonate proceeds in two phases (Houben, *Ber.*, 1903, xxxvi., 3087), *e.g.*,—

(1) $C_6H_5MgBr + Cl.COOC_2H_5 = C_6H_5.COOC_2H_5 + MgClBr,$

(2) $C_6H_5.COOC_2H_5 \rightarrow (C_6H_5)_3C.OH.$

Under suitable conditions, *i.e.*, by avoiding an excess of the Grignard reagent, ethyl benzoate is formed; so that we have here another method of converting bromobenzene into benzoic acid, in addition to the one which involves the use of carbon dioxide.

The following method has been applied for obtaining hydroxy-acids. The action of the Grignard reagent on the ester of a ketonic acid may be so regulated that the carbonyl group is attacked, whereas the —COOR group either survives the attack or is very slightly acted on; thus menthyl benzoylformate, $C_6H_5.CO.COOC_{10}H_{19}$, was converted by McKenzie (*Trans. Chem. Soc.*, 1904, lxxxv., 1261) into benzilic acid, $(C_6H_5)_2C(OH).CO_2H$, by means of magnesium phenyl bromide. The asymmetric synthesis of atrolactinic acid, $\frac{CH_3}{C_6H_5}>C<\frac{OH}{COOH}$, may be accomplished either from benzoylformic acid, $C_6H_5.CO.COOH$, or from pyruvic acid, $CH_3.CO.COOH$, by aid of the same reaction (McKenzie, *Trans. Chem. Soc.*, 1904, lxxxv., 1259; 1906, lxxxix., 365; McKenzie and Wren, *Ibid.*, 1906, lxxxix., 688).

Another example of a compound presenting two points of attack is afforded by ethylcyanoacetate. Here the —COOR group may survive the attack of the Grignard reagent, and by taking advantage of this Blaise was able to obtain esters of β-ketonic acids (*Comptes Rendus*, 1901, cxxxii., 38, 478, 978) :—

$$COOC_2H_5.CH_2CN + C_2H_5MgI \rightarrow COOC_2H_5.CH_2.C\overset{N.MgI}{\underset{C_2H_5}{=}} \rightarrow COOC_2H_5.CH_2.CO.C_2H_5.$$

(Compare Blaise's method for the preparation of ketones, see later).

(*b*) *Sulphur Acids.*—Sulphinic acids are formed by the action of sulphur dioxide (Rosenheim and Singer, *Ber.*, 1904, xxxvii., 2152), *e.g.*, benzenesulphinic acid is obtained from magnesium phenyl bromide :—

$$C_6H_5MgBr + SO_2 = C_6H_5.SO_2MgBr$$
$$C_6H_5.SO_2MgBr + H_2O = C_6H_5.SO_2H + MgBrOH.$$

Another method of obtaining sulphinic acids is described by Oddo, who uses sulphuryl chloride (*Atti R. Accad. Lincei*, 1905, [5], xiv., I., 169). Benzenesulphinic acid is produced according to the scheme :—

(1) $SO_2Cl_2 + C_6H_5MgBr = C_6H_5.SO_2Cl + MgClBr$
(2) $C_6H_5.SO_2Cl + C_6H_5MgBr = C_6H_5.SO_2MgBr + C_6H_5Cl$
(3) $C_6H_5.SO_2MgBr \rightarrow C_6H_5.SO_2H.$

Weigert (*Ber.*, 1903, xxxvi., 1007), shows that thiolic acids are obtained from carbonyl sulphide, which, *e.g.*, with magnesium ethyl bromide, gives thiolpropionic acid: $COS + C_2H_5MgBr = CS(C_2H_5).OMgBr \rightarrow C_2H_5COSH.$

Carbithionic acids are described by Houben and his pupils (*Ber.*, 1902, xxxv., 3696; 1906, xxxix., 3219; 1907, xl., 1303, 1725), who substitute carbon disulphide for carbon dioxide, thus: $CH_3MgI + CS_2 \rightarrow CH_3.CSSMgI \rightarrow CH_3.CSSH.$ Those interesting acids are yellow, red, or violet oils, rather unstable, strong acids, which are readily oxidised to the disulphides, R.CS.S.S.CS.R.

Ketones.

Nitriles were converted into ketones by Blaise, who obtains, *e.g.*, an 80 per cent yield of phenylethyl ketone from magnesium ethyl iodide and benzonitrile (*Comptes Rendus*, 1901, cxxxii., 38; cxxxiii., 299, &c.; compare also Béhal, *Bull. Soc. Chim.*, 1904, [3], xxxi., 461) :—

$$C_2H_5MgI + C_6H_5CN = C_6H_5.C\overset{C_2H_5}{=}N.MgI$$
$$C_6H_5.C\overset{C_2H_5}{=}N.MgI + H_2O = \frac{C_6H_5}{C_2H_5}>C:NH + MgIOH$$
$$\frac{C_6H_5}{C_2H_5}>C:NH + H_2O = NH_3 + C_6H_5.CO.C_2H_5.$$

The method, however, is not always so successful as in this particular case. Very varying yields were also obtained by Béis, who investigated the action on acid amides, which were heated for several hours with an excess of the reagent (*Comptes Rendus*, 1903, cxxxvii., 575). The action is represented as follows :—

$$R.CONH_2 + 2MgR'X = R.C(OMgX)(NHMgX)R' + R'H$$
$$R.C(OMgX)(NHMgX)R' + 2H_2O = R.C(OH)(NH_2)R' + MgX_2 + Mg(OH)_2$$
$$R.C(OH)(NH_2)R' = R.CO.R' + NH_3.$$

I have been able to find in the literature very few cases where ketones have been obtained from acid chlorides ; the latter, of course, readily yield tertiary alcohols. It is difficult to arrest the action in the first phase, $R'COCl + RMgX = R'.CO.R + MgXCl$. Acree obtains phenyl α-naphthyl ketone from benzoyl chloride and magnesium α-naphthyl bromide, but the yield is not stated (*Ber.*, 1904, xxxvii., 625). Gomberg and Cone obtain benzophenone in small yield from benzoylchloride and magnesium phenyl bromide (*Ber.*, 1906 xxxix., 2957).

Benzophenone may be obtained together with benzoic and triphenylcarbinol by the action of carbon dioxide on magnesium phenyl bromide, thus :—

$$C_6H_5MgBr \rightarrow C_6H_5.COOMgBr \rightarrow (C_6H_5)_2C(OMgBr)_2 \rightarrow (C_6H_5)_2CO$$

(Schroeter, *Ber.*, 1903, xxxvi., 3005 ; 1907, xl., 1584). But here, again, it has not been found possible to arrest the reaction so as to give a satisfactory yield of ketone. The method has also been applied by Bodroux for obtaining dibromo- and dichloro-derivatives of benzophenone (*Comptes Rendus*, 1903, cxxxvii., 710), but it cannot be quoted as a general method.

Kohler (*Am. Chem. Journ.*, 1904, xxxi., 642 ; 1905, xxxiii., 21, 35, 153, &c. ; *Ber.*, 1905, xxxviii., 1203 ; compare Bauer and Breit, *Ber.*, 1906, xxxix., 1916) finds on studying the action of unsaturated ketones that if a methyl group is attached to the carbonyl group of the ketone the reaction proceeds in the same manner as with a saturated ketone ; if, however, a phenyl group is attached to the carbonyl group, a ketone is produced. Thus cinnamylidene acetophenone, $C_6H_5.CH{:}CH.CH{:}CH.CO.C_6H_5$, does not form, with magnesium phenyl bromide, the tertiary alcohol $C_6H_5.CH{:}CH.CH{:}CH.C(OH)(C_6H_5)_2$, but gives β-phenyl β-styryl propiophenone,—

$$C_6H_5.CH{:}CH.CH(C_6H_5).CH_2.CO.C_6H_5.$$

Bauer (*Ber.*, 1904, xxxvii., 735 ; 1905, xxxviii., 240) obtains dialkylphthalides from phthalic anhydride ; thus with magnesium methyl-iodide :—

$$C_6H_4\langle^{CO}_{CO}\rangle O \rightarrow C_6H_4\langle^{C(CH_3)_2}_{CO_2H}\rangle OH \rightarrow C_6H_4\langle^{C(CH_3)_2}_{CO}\rangle O.$$

α-Methyl phthalide, $C_6H_4\langle^{CH(CH_3)}_{CO}\rangle O$, is obtained from phthaldehydic acid (Simonis, Marben, and Mermod, *Ber.*, 1905, xxxviii., 3981).

(To be continued).

Alloys of Cobalt and Tin.—F. Ducelliez.—From mixtures of cobalt and tin containing less than 57 per cent of tin, an alloy can be separated which approaches in composition to the compound Co_3Sn_2. This alloy is a powder which has not a very distinct crystalline character. It is attracted by a magnet. Its density is found to be 8·86, while the calculated density is 7·79. In chemical properties it resembles CoSn, but the latter appears to be more susceptible to the action of hydrochloric acid, while equally resistant towards nitric acid.—*Comptes Rendus*, cxlv., No. 8.

CORRESPONDENCE.

A WARNING.

To the Editor of the Chemical News.

Sir,—I shall be much obliged if, through the medium o your columns, you will allow me to put analytical chemists on their guard against a man who has recently been calling upon members of the profession with a view to monetary assistance, passing himself off under my name, and stating that he has had to resign the post of Public Analyst for Warrington as he is suffering from incurable consumption. It is a gross case of impersonation.—I am, &c.,

Frederick G. Ruddock,
Public Analyst for the Borough of Warrington.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

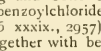
Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 7, August 12, 1907.

This number contains no chemical matter.

No. 8, August 19, 1907.

Symmetric Dimethyl Ethylene Oxide,—



—Louis Henry.—When methyl magnesium bromide acts upon symmetric dimethyl ethylene oxide, if the latter behaves like ethylene oxide, the product would be methyl isopropyl carbinol, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH—CH(OH)—CH_3$ (boiling-point 112°), but if the oxide isomerises a methyl ethyl ketone will be formed, giving rise to the tertiary alcohol, $(CH_3)_2=C—CH_2—CH_3$ dimethyl ethyl carbinol, $\quad\quad\quad

that of the substance NiSn. Thus, the general results of the author's work on these alloys are as follows:—Alloys of nickel and tin are magnetic when the percentage of tin lies between 0 and 40·22 (this number corresponding to Ni_3Sn); their brittleness increases as the amount of tin is increased, the maximum occurring between 40·22 (Ni_3Sn) and 66·76 (NiSn). After this it diminishes. At 85 per cent the alloys are to a certain extent malleable.

Action of Certain Substances upon Potassium Iodide.—B. Szilard.—Many substances, *e.g*, the oxides of uranium, thorium, iron, cobalt, &c., which are insoluble in water, have the power of acting on a solution of potassium iodide, setting free a certain amount of iodine; this reaction takes place even in an atmosphere of carbon dioxide. The same effect is produced by certain minerals, *e.g.*, fergusonite, cleveite, pitchblende. The degree of decomposition is very variable, and does not seem to be simply connected with the composition of the mineral. Certain uranium minerals (fergusonite, pitchblende) have a great activity, while others (thorianite, orangeite) have none at all. Joachimsthal pitchblende has the greatest activity, and with it contact is not absolutely necessary, for if paper is soaked in potassium iodide solution and starch, and placed above damp pitchblende in a closed vessel, it becomes blue. Pitchblende does not decompose potassium bromide or chloride, and experiments have shown that there is no connection between its radioactivity and its action on potassium iodide.

New Sensitive Method of Detecting Nickel.—Emm. Pozzi-Escot. — Nickel molybdate, obtained by the double decomposition of an alkaline molybdate and a nickel salt, is insoluble in a neutral or feebly acid aqueous solution which contains a sufficient excess of alkaline molybdate, while cobalt molybdate is very soluble under the same conditions. This reaction can therefore be used to detect nickel in presence of cobalt. Other metals, such as zinc, cadmium, manganese, also give a precipitate, but they can readily be eliminated by other methods. It is quite easy to detect 1 centigrm. of nickel in presence of five hundred times its weight of cobalt. The only case in which this method is not applicable is when the cobalt is present as a salt of cobaltamine, when it is at once precipitated; it must, however, be remembered that cobaltamine salts are readily converted into cobalt salts. The same method can be used for the microchemical detection of nickel, although zinc molybdate resembles the nickel salt closely.

Preparation of Asymmetric Halogen Hydrines and Properties of Corresponding Oxides of Ethylene.—MM. Fourneau and Tiffeneau.—The α-halogen hydrines can be prepared by the action of organomagnesium compounds upon either chloracetone chloracetic ether or their homologues. Mostly secondary products with boiling-points very close to those of the chlorhydrines are also formed, but the latter can be isolated by treating the raw product of the reaction either with potash, which converts the chlorhydrine into ethylene oxide, or with dimethylamine, which converts them into amino alcohols, soluble in acids. When an organo-magnesium derivative acts upon asymmetric disubstituted ethylene oxides the reaction which occurs may be represented by the equation $\begin{matrix} R \\ R \end{matrix}\!>\!C\!-\!CH_2 + BrMgR' \rightarrow RR\!=\!CH\!-\!CHOH\!-\!R'$.

With monosubstituted ethylene oxides the reaction is $R\!-\!CH\!-\!CH_2 + BrMgR' \rightarrow R\!-\!CHOH\!-\!CH_2\!-\!R'$.

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Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 12, 1907.

Use of Palladium as a Contact Substance in Elementary Analysis.—Arnold Jacobsen and Georg Landesen.—Palladium is more suitable for use as a contact substance in elementary analysis than platinum. It is readily oxidisable at a high temperature, and equally easily reduced when the temperature is further raised, or in presence of oxidisable substances; it removes the hydrogen from hydrocarbons at a red heat, depositing carbon, which may be completely burnt on the admission of air. The authors have found that it is best to use it in the form of asbestos, made by precipitating a solution of pure palladous chloride in presence of asbestos by sodium formate in alkaline solution, and then completely washing out the soluble salts. A potash glass tube of diameter about 1 cm. is drawn out so that a constriction with diameter about 0·5 cm. is made a few cm. from one end. The narrow part of the tube is filled with palladium asbestos, which is kept in place by a perforated clay plug. The substance to be burnt is placed in a porcelain boat behind the palladium asbestos, and the tube is connected with a gasometer containing oxygen. Before beginning the combustion the narrow part of the tube, and also the end which is to contain the porcelain boat, is heated. Then pure dry oxygen is led in, and the tube is allowed to cool; the boat is then introduced, and a current of oxygen allowed to pass, the palladium asbestos being meanwhile heated. The degree to which the part of the tube containing the boat is heated is regulated by the nature of the substance, and its volatility also decides the relative nearness of the boat to the asbestos, more volatile substances being placed further from the palladium, and care being taken that no condensation occurs between the boat and the palladium. The boat is preferably long and narrow in shape, and when the substance fuses before volatilising it must be evenly distributed throughout the boat. In the case of substances which are not very volatile, or volatilise with gradual decomposition, it is not necessary to use a tube with a constriction; equally good results being obtained with a tube which has not been drawn out.

Cobaltic Nitrites.—K. A. Hofmann and O. Burger.—When the aqueous solution of the cobalt ethyl ammonium salt, $[Co(NO_2)_6][AmH_3]$, is precipitated with excess of silver nitrate, and the dry silver salt is treated with ethyl iodide in dry ether, after warming for some time silver iodide separates, and ethyl nitrite results, while no nitroethane is formed. Hence, it may be deduced that the structure of the nitrous acid in the cobaltic nitrite is normal, but no definite proof of this is thus afforded. To prepare the nitrito-cobaltic acid ammonium, $[Co(NO_2)_6](NH_4)_3$, cobalt carbonate is suspended in 8 per cent aqueous ammonia, and the vapours from solid sodium nitrite and fuming nitric acid led in, meanwhile cooling with ice, until all the cobalt salt has disappeared; the liquid is dark brown, and the yellow salt is precipitated in considerable quantity. When this yellow salt, nitrito-cobaltic acid ammonium, is decomposed, it is found from the amount of nitrogen set free that it contains three normal nitrous acid residues bound to the ammonium. This result is completely confirmed by the investigation of the ethyl ammonium salt, $Co(NO_2)_6.(NH_3C_2H_5)_3$, which has now been prepared for the first time by leading nitrous acid gas into a cooled mixture of cobalt carbonate, water, and ethylamine solution.

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DIAMONDS.

A Lecture delivered before the British Association at Kimberley.

By SIR WILLIAM CROOKES,
Hon. D.Sc. (Oxford, Dublin, and Cape of Good Hope), F.R.S.

CHEMICAL NEWS OFFICE,
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THE CHEMICAL NEWS.

Vol. XCVI., No. 2497.

THE DEPOSITION OF METALLIC SILVER UPON GLASS.

Short Studies in Chemical History (II.).

By F. D. CHATTAWAY.

(Concluded from p. 153).

The glass speculum to be silvered, having been attached by pitch to a wooden block containing three eyes screwed into it by which it can be suspended face downward in the liquid, is next most carefully cleaned successively with strong nitric acid and caustic potash, and washed thoroughly with distilled water. It is then immersed in the silvering fluid face downwards, using so much fluid that a layer about half an inch in depth is interposed between its surface and the bottom of the vessel. When the silvering is complete, which will take from sixty to ninety minutes, according to the temperature, the speculum is removed from the solution, immediately washed with plenty of distilled water, and placed on its edge upon blotting paper to drain and dry.

When perfectly dry, the film is polished by gently rubbing with a piece of soft wash-leather, using circular strokes, and the operation is completed by the use of a little of the finest rouge.

When tarnished the brilliancy of the silver can be easily restored by re-polishing, and should the film of metal become detached or spoiled, it may easily be removed and a fresh one deposited without in any way impairing the figure or polish of the glass speculum. A plane surface can, of course, be silvered similarly.

Although Liebig's method of silvering glass was for a long time almost exclusively used in practice, a number of investigators busied themselves with the elaboration of new processes. These, however, differ from Liebig's, and also from each other, only in the agent used to reduce the dissolved silver oxide. Many substances have been recommended for the latter purpose, but only milk and grape-sugar, invert sugar, tartrates, aldehyde, ammonia, and formaldehyde have come into actual use.

The reducing liquid which has received the most extensive practical application in recent years is a solution of Rochelle salt, which has been mixed with a quantity of silver nitrate and boiled.

This solution was introduced by Dr. Ferd Bothe in preference to Rochelle salt itself (*Journ. Prakt. Chem.*, 1864, xcii., 191), though according to Claus (*Ber.*, 1875, viii., 948) it contains very little besides silver tartrate.

Bothe originally recommended that the reducing liquid should be prepared by precipitating silver tartrate, and boiling this with water, when blackening takes place, and the larger part goes into solution, forming a strongly reducing liquid. Bottger (*Polytech. Notizbl.*, 1864, 300) a few months later suggested that this liquid could be made more conveniently by adding a solution of silver nitrate to a hot solution of Rochelle salt, boiling the whole for about ten minutes, cooling, and filtering.

Kayser, in 1890 (*Zeit. Angew. Chem.*, 1890, 541), stated that, in spite of the greatly increased use of silver mirrors in recent years, no process had in practice proved invariably successful in producing large ones without flaws; he therefore gave the following detailed directions for the preparation and use of a mixed reducing solution which he had found to give uniformly good results.

To prepare the silver solution 10 grms. of silver nitrate are dissolved in 50 cc. of distilled water, and a pure solution of ammonia is dropped in till the precipitate first formed is just dissolved. Then, in order to avoid any excess of ammonia, a somewhat weak solution of silver nitrate is added until a slight opalescence appears, and the whole diluted to 1 litre. The solution is finally filtered, or, as is preferable, allowed to stand some time till it is quite clear.

To prepare the reducing fluid, 20 grms. of Rochelle salt and 20 grms. of pure white cane-sugar are dissolved in 200 cc. of distilled water, and a solution of 4 grms. of silver nitrate in 20 cc. of water added. The mixed liquids are shaken vigorously and boiled gently for half-an-hour; the hot mixture is then immediately diluted to 1 litre with cold distilled water, and, after well shaking, filtered.

For filtering purposes, equal volumes of the two liquids are mixed, and immediately poured on the plate to be coated, to a depth of from 1·5 to 2 cm. The deposition of silver begins almost at once, and is complete in from fifteen to twenty minutes. If the metallic film is not sufficiently thick the operation can be repeated. The plate, after thoroughly washing, is allowed to stand upright till completely dry. It may then be carefully varnished with a dilute alcoholic solution of shellac, and after this has thoroughly hardened, a second coat of a similar varnish, to which some indifferent colouring matter has been added, may be applied.

A very simple process, in which formaldehyde is used as the reducing agent, was described in 1894 by Auguste and Louis Lumière (*Séances de la Société Française de Physique*, 1894, 264). The silvering liquid used is prepared by dissolving 10 grms. of silver nitrate in a little water, adding ammonia drop by drop until the precipitate at first formed is re-dissolved, and diluting to 1 litre. As much of this as is necessary is mixed with half its volume of a 1 per cent solution of formaldehyde, prepared by diluting the commercial 40 per cent solution, and poured upon the surface to be silvered to a depth of 1 to 2 cm. After five to ten minutes at the ordinary temperature all the silver is deposited as a coherent layer which, after washing and drying, can be either polished or varnished.

Most of the processes which have been recommended will, if carefully carried out, give good results, and it appears largely a matter of preference which should be adopted for any purpose.

Ostwald and Luther in their "Hand- und Hülfsbuch zur Ausführung Physiko-Chemischer Messungen (Leipzig, 1902) recommend a modification of a method proposed by Adolphe Martin in 1868 (*Ann. de Chim. et de Phys*, 1868, [4], xv., 94), and give the following instructions:—"Dissolve 90 grms. of pure sugar in a litre of water, and add to it 175 cc. of alcohol and 4 cc. of nitric acid of density 1·2. Allow the solution to stand for at least a week before use. Shortly before it is required dissolve 1 grm. of silver nitrate in 100 cc. of distilled water, add 1 cc. of a strong solution of ammonia of density 0·9, and then, drop by drop shaking continuously, a more dilute solution of ammonia (about 1 volume concentrated solution of ammonia and 5 volumes of water) until the precipitate is just dissolved. Add then half a gram of caustic potash (purified by alcohol and as far as possible free from carbonate) dissolved in 50 cc. of water, and again drop in cautiously the diluted solution of ammonia until nearly all the re-precipitated oxide disappears. Allow the slightly cloudy brownish coloured liquid to stand for some time, and filter through cotton-wool.

"In order to carry out the silvering mix 150 cc. of the silver solution with 6 cc. of the sugar solution, and pour it over the surface to be covered. One grm. of silver nitrate is sufficient to silver 40 square centimetres. At a temperature of about 20° C. the reduction is completed in ten to fifteen minutes. When the deposition of silver is finished the plate should be throughly washed with water and carefully dried. It may afterwards be polished if it is desired that it should reflect from the metallic surface."

The successful silvering of glass depends above everything upon the perfect polish and cleanliness of the surface. Blown glass which has not been touched can be silvered much more easily than polished. If the glass has been

kept for any length of time it will not take the silver properly without re-polishing. The surface immediately before silvering should be throughly washed, using in succession hot soap solution, strong nitric acid, and a strong solution of caustic potash. The surface should be thoroughly rubbed with each liquid by means of a pad of cotton-wool tied to a glass rod, or better partially thrust tightly into one end of a glass tube. Between each successive cleansing the plate should be thoroughly washed with clean water, and just before being placed in the silvering fluid it should be well rubbed over with it and wetted in every part, using a pad of cotton-wool soaked with the liquid.

The purity of the materials employed is also of the highest importance. Chlorides, either in the chemicals or in the water used, are especially to be avoided. The alkali, both the ammonia and the potash, must be as far as possible free from carbonate, as the latter is found to cause considerable reduction to take place in the bath itself, and thus to diminish the quantity of silver deposited upon the glass; it also appears to produce upon the silvered surface white flecks which cannot be removed.

The surface after silvering must be very carefully washed, as if the last traces of the silvering fluid are not removed they are liable to cause stains and defects to develop later in the mirror.

The film of silver must on no account be touched until it is perfectly dry, and even after drying and polishing it is always very sensitive to damp. The specula of reflecting telescopes, for example, if they have been exposed to damp air or dew, should always be dried in the most thorough manner before they are re-polished or touched in any way.

When a large surface has to be silvered, as in the manufacture of mirrors, the plate having been carefully levelled, the silvering fluid is poured directly upon it, the surface tension being sufficient to prevent a layer of the depth required running off at the edges. The room where the glass is silvered must be kept free from all dust, and its temperature should not be allowed to fall below 20° C.

Although silvered glass mirrors, when properly made, are far more durable than mercurial mirrors, and reflect much better with a loss of only about 10 per cent of the light falling upon them, they yet possess one property, which is sometimes regarded as a defect. Like mirrors of polished silver, they show the slightest trace of a yellow colour. It is, of course, impossible to avoid this when silver is used. If one looks at the sun through a thin deposit of silver upon glass, its disc appears of a blue colour, while if the layer is very thin it is as though one looked through blue glass. Silver therefore allows blue rays to pass through and become absorbed, while light of other refrangibilities is reflected. White light when reflected from a silver surface must therefore lose a certain proportion of its blue rays, and since the yellow rays are no longer completely compensated the reflected light has a slightly yellow colour. A yellowish tint is thus given to any white object seen mirrored in silver.

This supposed defect has prevented to a large extent the replacement of mercurial by silvered mirrors in France, and attempts have been made to overcome it by treating the film of silver deposited in the ordinary way with various mercury salts, and thus converting it into amalgam.

Drautz has suggested another method, and in 1891 patented a process (D.R.P. 56,260) for obtaining a silver deposit with a bluish tint by using a reducing solution containing a little of a lead salt.

In spite of the large amount of work which has been done on the reduction of silver salts in connection both with mirror making and with photography, very little is known as to the reason why, when silver oxide is reduced under certain conditions, the metal is deposited on the glass in the form of a brilliantly reflecting coherent film, while under others apparently equally favourable to such deposition it separates in a spongy or flocculent state.

Vogel (*Journ. Prakt. Chem.*, 1862, lxxxvi., 321) concludes from his experiments that when complete reduction of the oxide takes place in one stage, a mirror or a crystalline deposit of silver is obtained, while granular or finely divided silver is produced in two stages, a lower insoluble oxide of silver separating as the primary product of the reduction and being afterwards itself reduced.

The assumption of reduction in two stages appears, however, unnecessary, and in no way explains the circumstance that mirrors are never formed, or only with great difficulty, in an acid solution. For the silver to separate entirely on the surface of the glass it is necessary for it to be deposited from a clear solution containing no metallic particles to act as nuclei for deposition in the body of the liquid, nor any solid particles of oxide able on reduction to form such.

It seems probable that an explanation must be sought in some catalytic action of the glass surface which locally accelerates reduction in alkaline solution.

Oberbeck some years ago (*Ann. der Physik. und Chem.*, 1892, xlvi., 265) measured the electric resistance of a thin mirror of silver deposited from aqueous solution upon glass. His results show that the electric resistance of such films is very large immediately after deposition, but that it continually diminishes with time, and has not reached a minimum even after two years. He notes that this diminution in the resistance takes place whether the films are thick with a good reflecting surface or thin and semi-transparent. The actual resistances of the different films measured by Oberbeck varied originally from 19·7 ohms to 633·7 ohms, the resistances of this pair of films diminishing in 641 days to 2·84 and 58·4 ohms respectively.

In spite of such great alterations in resistance the mirrors showed no change either in reflecting power or in appearance when viewed by transmitted light.

Oberbeck concluded that his observations could only be explained by assuming that the silver so deposited is, when first laid down, in a different molecular condition from ordinary silver, but that its condition approaches that of the latter more and more with time.

SIMPLE MODELS OF TETRAHEDRAL CARBON ATOMS.

By R. V. STANFORD, M.Sc.

Both for lecture demonstration and for the study of stereochemical questions the possession of a set of models of tetrahedral carbon atoms is of great convenience to the chemist. Such models are readily constructed in any number in the following way:—

A piece of close-grained wood, such as canary wood, is planed into a strip of triangular section, each side being 2 cm. wide. One end is "squared," and a line is cut round the strip 1·63 cm. from this face. The middle point of the triangular end-face is then found and marked with a pencil point, and each side is cut down to it from the line. In this way three of the sides of a regular tetrahedron are produced. The tetrahedron is now sawn off the strip and the remaining face produced by cutting down to the mark previously made round the strip.

Some thin steel-wire is then taken—that used for making wire-brushes is convenient—and cut into 3 cm. lengths, which are driven into the tetrahedron at the corners with the aid of a pair of pliers. Care should be taken that the wires are so inserted as to be perpendicular to the opposite faces of the tetrahedron.

In constructing the space model of a compound with these atoms the bonds are united by means of small pieces of cork, and the atoms are so light that quite complicated models may easily be built up with them. Owing to the elasticity of the steel-wires, they are also well adapted for showing the applicability of Baeyer's tension theory to the polymethylene derivatives; a trimethylene ring, for instance, splits instantly apart when one of the uniting corks is somewhat loosened.

Chemical Department, University of Birmingham.

ON THE DENSITY CURVE OF MIXTURES OF BROMINE AND CHLORINE.*

By LAUNCELOT W. ANDREWS and HENRY A. CARLTON.

THE fullest determinations of the densities of bromine at various temperatures appear to be those of Thorpe (*Journ. Chem. Soc.*, 1880, xxxvii., 172) and of Pierre (Moissan, "Traité de Chimie Minérale," i., 133; *Ann. Chim. Phys.*, 1847, [3], xx., 45). The former determined the density at 0° to be 3·187, while Pierre found at the same temperature 3·188. At 35° Thorpe found 3·10104 and Pierre 3·10472 (Interpolated). We shall bring forward evidence in the present paper going to show that the results of Thorpe are too low by an amount which can be accounted for on the assumption that his bromine contained about 0·039 per cent of chlorine. The density of liquid chlorine at 25°, as calculated from the formula of Knietsch, is 1·39778 (*Annalen*, 1890, cclix., 100). The existence of a monochloride of bromine is generally assumed, on the basis of the investigations of Bornemann (*Annalen*, 1877, clxxxix., 206). There seems to be but little evidence to support this assumption, except the existence at low temperatures of hydrates, said to have the formulæ $BrCl.5H_2O$ and $BrCl.10H_2O$ (Loewig, "Das Brom," 64, Heidelberg, 1829). Obviously the existence of such hydrates, even if fully demonstrated, would constitute no sufficient proof of the existence of the compound BrCl in the absence of water. Proof or disproof of the existence of compounds of chlorine and of bromine with one another must be sought for in the physical properties and behaviour of mixtures of these elements at ordinary or at low temperatures. Among the properties to be taken into consideration in this connection is that of density. If it should appear that these elements mix without contraction of volume, that fact alone would be strong presumptive evidence against the existence of a compound. The chief object with which the authors undertook an investigation of the density curve of chlorine-bromine mixtures was a purely practical one. A simple preliminary calculation showed that, unless a very considerable contraction occurs on mixing chlorine with bromine, small percentages of chlorine must so greatly reduce the density of bromine as to make it possible to base on the density alone a determination of the chlorine with the prospect of very satisfactory results. This anticipation was fully realised.

In the density determinations three pycnometers were used by the authors, of which two were of the well-known Squibb type, with narrow divided stem, ground into the body, of 50 and 25 cc. respectively.

The values of the stem divisions were found by calibration with mercury, the capacity of the bulbs by weighing with water. The third instrument, made by Koehler, of 35 cc. capacity (nominal), is a constant volume instrument with the thermometer fused in the bulb. The readings of this, as of all other thermometers used, were carefully controlled.

It was not found possible by re-grinding the joints of the Squibb pycnometers to absolutely prevent evaporation of bromine. The loss was, however, small and was checked by weighing both before and after acquiring the temperature at which the scale reading was taken. It was observed that in two of these instruments the weight of the bromine caused the bottom of the bulb to bulge a little, increasing the volume above what it was when calibrated with water. The amount of this error was determined by immersing the pycnometer, filled with bromine, in a liquid of about the same density (acetylene tetrabromide) and comparing the reading with that obtained when the instrument was immersed in water, both liquids being in the same thermostat at identical temperatures. The maximum error due to this cause amounted to about five units in the fifth decimal place. No attempt was made to correct for it. If greater accuracy should be aimed at in future work, only pycnometers of spherical form, made rather thick in the wall and not flattened at the bottom, should be used. Very accurate thermometer readings would then become necessary. Some of the determinations referred to below were made at various temperatures between 25° and 32°. Those which were relied on for determinations of the constants of the formula were made in a thermostat within a few tenths of a degree of 25°, so that the correction for reduction to this temperature was small.

The weights used were corrected by comparison with a set of which a table of corrections had recently been furnished by the Bureau of Standards. Two thermometers were used. Their readings were reduced to the international hydrogen standard, on the basis of comparison with an instrument standardised by the Reichsanstalt and further controlled by observations at the zero point and at the transition point of sodium sulphate (after Richards). Both harmonised well. They were divided into one-fifth degree, but were read with a glass to one-fiftieth, with a probable error of about this amount. In consequence of the high coefficient of expansion of bromine, uncertainties in the temperature determinations become the chief source of error and practically set the limit to the accuracy of the results obtained.

The apparent coefficient of expansion of bromine in glass over the range 25° to 30° was found by us to be 0·00110, in excellent agreement with the results of Thorpe (*loc. cit.*). This factor was used in reducing observations made at other temperatures to the 25° standard, and we have assumed it to be valid for the impure as well as for the pure bromine. That this assumption is not too far from the truth within the limits of concentration to which it was applied is confirmed by a single determination of the coefficient for a bromine containing about five per cent of chlorine, which gave the value, 0·001128.

The density of pure bromine was determined on four preparations made from material derived from different sources and purified by different methods. The results are: Series A, 3·1022, 3·1019, 3·1022, 3·1019; Series B, 3·10143: Series C, 3·10218, 3·10230; Series D, 3·1025, 3·1027, 3·1025. Preparation B was partially frozen (melting point, −7·1°), the liquid portion poured off and the crystals used for the determination. An accident prevented its further examination, but although the density found is certainly too low, the figures are given, since the cause of the error is unknown. Series D is regarded as the most reliable, because the temperature determinations are more precise, the temperature corrections much smaller, and, further, because the material was shaken with calcium carbonate to remove possible traces of hydrobromic acid. In series A the bromine was dried with sulphuric acid, in the other series with phosphoric anhydride. Preparations A and D were known to be chlorine-free. They were tested by the method recently given by one of us (*Journ. Am. Chem. Soc.*, xxix., 275). Equal confidence is felt that Preparations A and B were also free from chlorine because of the guarantee afforded in the light of our experience with the method of preparation employed. The melting-point of Preparations A, C, and D was 7·0°, and the boiling-point 58·7° at 763 mm.

Probably the most persistent contamination of bromine is hydrobromic acid. We have not been able to devise any method for its removal which is not open to criticism. It should be said that Preparation D, after drying, &c., was re-distilled in two large fractions and a third, smaller, one. The first two had identical densities, the third a slightly lower one. Perhaps it is permissible to assume that all or a great part of the hydrobromic acid originally present was concentrated in the last fraction.

If double weight is assigned to Series D, and the one doubtful observation of Series B is not omitted from consideration, we obtain as the most probable value of the density of pure dry bromine from our observations $D\ 25°/4° = 3·10227$. With the aid of this constant for bromine and of the corresponding figure for chlorine of

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Knietsch previously referred to, the theoretical relation of chlorine percentage (p), in a mixture of the two elements, to the density at 25° (d) of the mixture is given by the formula—

$$p = 82{\cdot}005\left(\frac{3{\cdot}10227}{d} - 1\right) \quad . \quad . \quad . \quad . \quad 1$$

on the assumption that no contraction occurs. We find that an expression of the same form, with a change in the coefficient of the second term, reproduces the observation values very well; to wit—

$$p = 88{\cdot}593\left(\frac{3{\cdot}10227}{d} - 1\right) = \frac{274{\cdot}840}{d} - 88{\cdot}593. \quad . \quad 2$$

When the mixture is saturated with water, the formula becomes—

$$p = 88{\cdot}59\left(\frac{3{\cdot}1004}{d} - 1\right) = \frac{274{\cdot}665}{d} - 88{\cdot}59 \quad . \quad . \quad 3$$

The last expression (3) must be regarded as merely approximate in character, since, as is well known, bromine and water react, producing hydrobromic acid and hypobromous acid. Hence, with the duration of contact the apparent solubility of water in the bromine steadily increases. When the relative amount of water is small the phenomenon is most marked, and the density of the bromine continues to decrease for a long time as it takes up hydrobromic acid and water. Equation 3 is approximately correct for bromine which has been quickly saturated at 25° with water by violent shaking.

The degree of precision of Equation 2 when applied to mixtures of pure bromine with pure chlorine is shown by the following comparison of the chlorine percentages of such mixtures as deduced by analysis (*Journ. Am. Chem. Soc.*, xxix., 275), and as calculated by the formulæ from the observed densities.

Per cent by analysis.	Density dry.	Per cent by Equation 2.	Density wet.	Per cent by Equation 3.
4·388				
4·461				
4·439	2·9553	4·406	2·9535	4·406
4·442				
4·407				
4·401				
7·741	2·8533	7·730	2·8512	7·743
7·717				
7·198			2·8661	7·242

The organic and other impurities, aside from chlorine, which are usually present in crude bromine, do not very seriously influence the results of the density determinations, as may be seen from the following analyses of material of this sort.

	1.	2.	3.	4.	5.	6.
Per cent of Cl—						
By density .	4·137	0·070	5·485	0·000	4·294	6·06
By analysis.	4·165	0·051	5·580	0·012	4·400	6·22

It is possible, therefore, to determine from the density of a sample of bromine the amount of chlorine it contains with sufficient accuracy for almost any purpose and in much less time than by any chemical method.

The contraction that occurs on mixing (liquid) chlorine with bromine can be readily calculated from Equation 2. The validity of this formula has only been tested to 11 per cent of chlorine, but if we extrapolate to 30 per cent (corresponding in composition approximately to BrCl) it gives for the corresponding density 2·4175, whereas, if no contraction occurred the density would be 2·2713. The contraction amounts, accordingly, to about 2 per cent of the total volume, a result that appreciably increases the probability that actual chemical combination does take place between these elements to a limited extent.

In conclusion, we present the following comparison of the densities of bromine at several temperatures as found by Thorpe and by Pierre with our own results.

Temp. °C.	Pierre (1847).	Thorpe (1880).	A. and C. (1906).
0	3·188	3·187	—
20	3·121(45)	3·118(43)	3·11932
25	3·104(72)	3·101(04)	3·10227
30	—	—	3·08479

ON THE

ARSENATE PROCESS FOR THE SEPARATION OF MAGNESIUM AND THE ALKALIS.

By PHILIP E. BROWNING and W. A. DRUSHEL.

Among the methods which have been employed for the separation of magnesium from the alkalis the following are perhaps in most general use:—

The barium hydroxide method, whereby the magnesium is precipitated as the hydroxide by barium hydroxide.

The mercuric oxide method, whereby the magnesia is precipitated by freshly prepared mercuric oxide acting upon the chlorides.

The ammonium carbonate method, whereby the magnesium is precipitated as the double carbonate of magnesium and ammonium by a large excess of ammonium carbonate (Wulfing, *Ber.*, xxxii., 2214).

The amyl alcohol method, whereby the magnesium chloride is dissolved in boiling amyl alcohol and the chlorides of sodium and potassium, not lithium, remain undissolved (Riggs, *Am. Journ. Sci.* [3], xliv., 103).

None of these methods, when employed with a view to the subsequent estimation of the alkalis, is free from objectionable features, such as difficulties of filtration, numerous transfers of filtrates, introduction of large amounts of reagents difficult of removal, and incomplete separation of the entire alkali group.

The work to be described is an effort to avoid some of the objections mentioned, by the precipitation of magnesium as the magnesium ammonium arsenate and the removal of the arsenate from the filtrate by reduction and volatilisation of the arsenic salt. C. v. Hauer (*Jahrb. der k. k. Geolog. Reichanstalt*, iv., 863) suggested this general procedure and it has found other mention in the literature (Fresenius-Cohn, "Quant. Anal.," 6th ed., vol. i., 613). The removal of the excess of arsenic was accomplished by ignition of the residue, obtained after evaporating the filtrate from the ammonium magnesium arsenate, with ammonium chloride. The method, however, has been criticised as inaccurate for the estimation of magnesium, and tedious. Recent work upon the precipitation of magnesium ammonium arsenate and upon the volatilisation of arsenic compounds suggested the possibility of obviating the difficulties which have kept this method from general use.

It is possible, with careful manipulation, to remove the arsenic by precipitating with hydrogen sulphide, but this procedure required an additional filtration and several transfers of liquid, and was therefore abandoned in favour of the separation by volatilisation.

The reagents used in this work were prepared as follows: The potassium chloride by igniting pure potassium chlorate and crystallising; the sodium chloride by re-crystallising the so-called pure sodium chloride. Solutions of these salts were made approximately tenth normal and standardised by evaporating measured portions with sulphuric acid in a weighed platinum crucible, and weighing the residues after ignition at the full heat of a Bunsen burner, as the normal sulphates.

A solution of magnesium chloride was obtained by dissolving a weighed amount of pure magnesium in hydrochloric acid and diluting sufficiently to make the solution approximately tenth normal. The solution was standardised by estimating the magnesium in measured portions as the pyroarsenate.

To obtain ammonium arsenate, arsenious oxide was sublimed and oxidised by an access of nitric acid. After

Table II.

	$(NH_4)_3AsO_4$ used, calculated as As_2O_5.	Dilution.	NaCl or KCl converted to Na_2SO_4 or K_2SO_4 and calculated as Na_2O or K_2O.			$MgCl_2$ converted into $Mg_3As_2O_7$ and calculated as MgO.		
			Taken.	Found.	Error.	Taken.	Found.	Error.
	Grm.	Cc.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·1	100	0·1194	0·1191	−0·0003	0·0199	0·0197	−0·0002
2.	0·2	150	0·1194	0·1196	+0·0002	0.0399	0·0397	−0·0002
3.	0·45	250	0·1194	0·1195	+0·0001	0·0998	0·0998	—
4.	0·45	250	0·1194	0·1194	—	0·0998	0·0997	−0·0001
5.	0·45	250	0·2389	0·2385	−0·0004	0·0998	0·0999	+0·0001
6.	0·4	250	0·0478	0·0481	+0·0003	0·1198	0·1193	−0·0005
7.	0·35	250	0·0956	0·0957	+0·0001	0·0998	0·0996	−0·0002
8.	0·35	250	0·0956	0·0957	+0·0001	0·0998	0·0994	−0·0004
9.	0·45	250	0·0909	0·0915	+0·0006	0·0998	0·0993	−0·0005
10.	0·1	100	0·0545	0·0549	+0·0004	0·0006	0·0004	−0·0002
11.	0·1	100	0·1181	0·1184	+0·0003	0·0040	0·0038	−0·0002
12.	0·1	100	0·1181	0·1184	+0·0003	0·0040	0·0038	−0·0002
13.	0·1	100	—	—	—	0·0040	0·0038	−0·0002
14.	0·1	100	0·1181	0·1184	+0·0003	0·0040	0·0040	—
15.	0·2	100	0·1181	0·1183	+0·0002	0·0040	0·0039	−0·0001
16.	0·45	250	0·1181	0·1179	−0·0002	0·1002	0·1004	+0·0002

the completion of the oxidation, the excess of nitric acid was removed by evaporation, the residue treated with a slight excess of ammonium hydroxide, and the solution thus obtained diluted sufficiently to make it approximately fifth normal.

From a mixture of known amounts of standardised solutions of the chlorides of magnesium and potassium or sodium, the magnesium was precipitated in a distinctly but not strongly ammoniacal solution by 40 per cent to 80 per cent excess of ammonium arsenate, with brisk stirring. When only a small amount of magnesium is present in a relatively large amount of solution, the precipitate forms slowly and becomes complete only on long standing. In a previous paper from the Kent Chemical Laboratory of Yale University (Gooch and M. A. Phelps, *Am. Journ. Sci.*, 1906, xxi., 488), it has been shown that the precipitation of amounts of arsenic so small as not to be precipitated immediately by magnesium mixture may be brought about by freezing the solution after adding that reagent, and remains complete when melting takes place. This procedure was found equally applicable in the precipitation of magnesium. A similar result was obtained by adding alcohol amounting to 15 per cent to 20 per cent of the mixture and filtering as soon as the precipitate settled completely. The precipitate was collected under moderate pressure in an ignited and weighed perforated crucible containing a close felt of fine asbestos. It was washed with 40 to 50 cc. of ammoniacal water, after which it was dried at 125° C. to 140° C. and carefully ignited and weighed as magnesium pyroarsenate.

In a previous paper from the same laboratory, it has been shown that arsenic may be removed by distillation with potassium bromide and hydrochloric acid in a distilling apparatus (Gooch and I. K. Phelps, *Am. Journ. Sci.*, 894, xlviii., 216). This suggested a method for the removal of the arsenic from the filtrate obtained after separating the magnesium ammonium arsenate. In some preliminary qualitative experiments, solutions containing from 0·1 to 0·2 grm. of ammonium arsenate were treated with 10 cc. of hydrochloric acid (sp. gr. 1·20) and 10 cc. of hydrobromic acid (sp. gr. 1·36), or 1 to 3 grms. of ammonium bromide, and evaporated in an open dish and the residues were ignited until fuming ceased. One such treatment was usually found to be sufficient ; in fact, simple evaporation on a steam bath with the mixed acids, or with hydrobromic acid (not with hydrochloric acid alone), proved to be sufficient to remove the arsenic. Similar treatments made in the presence of definite amounts of the sodium or potassium chloride gave the results shown in Table I.

Table I.

	Ammonium arsenate calculated as As_2O_5.	NaCl or KCl converted to Na_2SO_4 or K_2SO_4 and calculated as Na_2O and K_2O.		
		Taken.	Found.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0·2	0·1171	0·1172	+0·0001
2.	0·2	0·1171	0·1170	−0·0001
3.	0·4	0·1873	0·1870	−0·0003
4.	0·2	0·0468	0·0473	+0·0005

Some evaporations made with hydrochloric acid and sulphurous acid resulted in the removal of the arsenic, but three to five repetitions of the process were generally necessary.

The complete method as recommended for the estimation of magnesium and its removal from the alkalis, and the subsequent estimation of the alkalis, is as follows :—

The magnesium is precipitated in a distinctly but not strongly ammoniacal solution by a 40 per cent to 80 per cent excess of ammonium arsenate. The completeness of the precipitation may be hastened by freezing the solution in an ice and salt mixture or by adding alcohol to about 15 per cent to 20 per cent of the total volume of the solution, which may vary from 100 cc. to 250 cc. according to the amounts of salt present. The magnesium arsenate obtained is filtered on an asbestos felt contained in a perforated platinum crucible, the crucible and felt having been previously ignited and weighed, and is dried, ignited, and weighed as the pyroarsenate.

The filtrate is transferred from the filter flask to a platinum dish, and after the addition of 10 cc. of hydrochloric acid (sp. gr. 1·20) and about the same amount of hydrobromic acid (sp. gr. 1·3), or 1 to 3 grms. of ammonium bromide evaporated to dryness under a draught-hood, the residue is gently ignited to remove the ammonium salts. The residue is then transferred to a weighed platinum crucible with a small amount of water, a little sulphuric acid (1 : 1) added, and the solution evaporated to remove the water and excess of sulphuric acid, by placing the crucible on a triangle in a porcelain crucible used as a radiator. After the sulphuric acid has ceased to fume, the crucible is removed from the radiator, and after ignition at the full heat of the Bunsen burner the alkali is weighed as the normal sulphate. The results are given in Table II.

In experiments 1 to 10, the precipitate of magnesium was allowed twelve to twenty-four hours to settle. In experiments 11, 12, and 13, 15 per cent alcohol was used to hasten the complete precipitation of the magnesium,

and in experiments 14, 15, and 16 the salt and ice mixture was used for the same purpose.—*American Journal of Science*, xxiii., p. 293.

THE

APPLICATIONS OF GRIGNARD'S REACTION.*

By ALEX. McKENZIE, M.A., D.Sc., Ph.D.

(Continued from p. 161).

Section I. (*continued*).

Aldehydes.

Aldehydes are obtained, according to Bouveault (*Comptes Rendus*, 1903, cxxxvii., 987), from disubstituted formamides :—

$$H.CONRR' + R''MgX - HCR''(OMgX).NRR'$$

$$HCR''(OMgX).NRR' + H_2O = = R''.CHO + NHRR' + MgXOH.$$

Benzaldehyde, for example, was formed from ethyl formanilide and magnesium phenyl bromide.

Bodroux prepared a number of aldehydes in satisfactory yields from ethyl orthoformate (*Comptes Rendus*, 1904, cxxxviii., 92, 700; compare Tschitschibabin, *Ber.*, 1904, xxxvii., 186, 850). Benzaldehyde, for example, was obtained in a 90 per cent yield :—

$$CH(OC_2H_5)_3 + C_6H_5MgBr = MgBr(OC_2H_5) + C_6H_5.CH(OC_2H_5)_2$$

$$C_6H_5.CH(OC_2H_5)_2 + H_2O + HCl = = 2C_2H_5OH + HCl + C_6H_5.CHO.$$

After Grignard had shown that secondary alcohols are formed from magnesium organic compounds (2 mols.) and formic esters (1 mol.), Gattermann and Maffezzoli (*Ber.*, 1903, xxxvi., 4152; compare Farbenfabriken vorm F. Bayer and Co., D.R.P., 1904, 157573) obtained aldehydes from magnesium organic compounds (1 mol.) and formic esters 3 mols.); secondary alcohols are formed at the same time, and the yields of aldehydes are not particularly good. The formation of *o*-toluyl aldehyde from *o*-bromotoluene is represented as follows :—

$$CH_3.C_6H_4.MgBr + H.COOC_2H_5 = = BrMg.OC_2H_5 + CH_3.C_6H_4.CHO.$$

Gattermann (*Annalen*, 1906, cccxlvii., 347; compare Monier Williams, *Trans.*, 1906, lxxxix., 273) shows that ethoxymethyleneaniline may be used in place of ethyl formate; anils are then formed from which aldehydes are obtained by the action of mineral acids, thus—

$$C_6H_5.N:CH.OC_2H_5 + RMgBr = = C_6H_5.N:CHR + C_2H_5OMgBr$$

$$C_6H_5.N:CHR + H_2O - R.CHO + C_6H_5.NH_2.$$

Sachs and Loevy (*Ber.*, 1904, xxxvii., 874) find that additive compounds are formed from *iso*nitriles, for which Nef's formulation, R.N:C, is taken. These additive compounds, $R.N:C<^{Aryl}_{Mg.Br}$, when treated with mineral acids probably give first aldehydeimide derivatives, R.N:CH.Aryl, and then aldehydes, O:CH.Aryl. The method, however, is not a very practical one.

Ethers.

Klages (*Ber.*, 1904, xxxvii., 3987) has prepared a number of phenol ethers from aldehydes; for example, *o*-propenyl phenetole, $C_2H_5.O.C_6H_4.CH:CH.CH_3$, from ethyl salicylaldehyde and magnesium ethyl iodide.

According to Hamonet (*Comptes Rendus*, 1904, cxxxviii., 813, 975; 1904, cxxxix., 59), halogen-substituted methyl ethers interact with magnesium organic compounds, thus : $RMgX + XCH_2OR = MgX_2 + R.CH_2OR$.

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

Esters.

According to Grignard (*Comptes Rendus*, 1902, cxxxiv., 849), monoethyl ethylacetoacetate interacts with magnesium methyl iodide, partly in accordance with its ketonic structure, $CH_3.CO.CH(C_2H_5).COOC_2H_5$, to give the ester $(CH_3)_2C(OH).CH(C_2H_5).COOC_2H_5$.

Ethyl chlorocarbonate can be converted into ethyl benzoate by means of magnesium phenyl bromide when care is taken to avoid an excess of the latter by dropping it into an excess of the chlorocarbonate, thus : $C_6H_5MgBr + Cl.CO_2C_2H_5 = C_6H_5.COOC_2H_5 + MgClBr$ (Houben, *Ber.*, 1903, xxxvi., 3087). The reaction appears to be a general one.

Ethyl benzoate may also be prepared from magnesium phenyl bromide by a method described by Tschitschibabin (*Ber.*, 1905, xxxviii., 561), who uses normal carbonic esters :—

$$RMgX + CO(OC_2H_5)_2 - RC(OMgX)(OC_2H_5)_2$$

$$RC(OMgX)(OC_2H_5)_2 + H_2O = = R.COOC_2H_5 + C_2H_5OH + MgXOH.$$

If the reaction between magnesium organic compounds and orthocarbonic esters is moderated and not too prolonged it proceeds thus :—

$$C(OC_2H_5)_4 + RMgX = R.C(OC_2H_5)_3 + MgX(OC_2H_5).$$

Houben describes a method for the preparation of esters from alcohols or phenols (D.R.P., 1905, 162863; *Ber.*, 1906, xxxix., 1736). The alcohol or phenol is converted, by means of magnesium alkyl chloride, into its magnesium chloro-compound, which is then caused to interact with an acid chloride or anhydride, *e.g.*, with benzyl alcohol :—

$$C_6H_5.CH_2OH + C_2H_5MgCl = C_6H_5CH_2OMgCl + C_2H_6$$

$$C_6H_5CH_2OMgCl + (CH_3CO)_2O = = C_6H_5CH_2OCOCH_3 + CH_3.COOMgCl.$$

The preparation of the acetates of terpineol, linalool, thymol, and *cis*-terpin is described. The method gives excellent yields, and appears to be particularly suitable for the preparation of esters from unstable tertiary alcohols.

Nitrogen Compounds.

In continuation of his work on the formation of ketones from nitriles, Blaise (*Comptes Rendus*, 1901, cxxxii., 38, 478, 978) describes the preparation of anilides from phenyl *iso*cyanate, thus :—

$$C_6H_5.N:C:O + RMgI = C_6H_5.N:C<^{OMgI}_{R} \rightarrow$$

$$\rightarrow C_6H_5.N:C<^{OH}_{R} \rightarrow C_6H_5NH.COR.$$

Another method of obtaining anilides is given by Bodroux (*Comptes Rendus*, 1904, cxxxviii., 1427), who uses the magnesium organic compounds of primary aromatic amines. This type, RNHMgI, is obtained either by adding the amine to a cold ethereal solution of magnesium methyl iodide, or by the action of equimolecular amounts of methyl iodide and amine on magnesium in the presence of ether. When an ester of a monobasic acid is then added, and the product decomposed as usual by dilute acid, an almost theoretical yield of anilide is obtained :—

$$2RNHMgI + R'.COOR'' = MgIOR'' + R'.C(NHR)_2.OMgI,$$

$$R'.C(NHR)_2.OMgI + HCl = = R.NH_2 + MgICl + R'.CO.NHR.$$

The action of magnesium organic compounds on mustard oils is analogous to the action on *iso*cyanates. Sachs and Loevy (*Ber.*, 1903, xxxvi., 585; 1904, xxxvii., 874) obtained a number of thioanilides according to the scheme—

$$R.N:C:S + R'MgI = R.N:C(R').S.MgI$$

$$R.N:C(R').S.MgI + HCl = R.NH.CSR' + MgCII.$$

Nitrosohydroxylamines are formed by the action of nitric oxide on the Grignard reagent, nitrosophenylhydroxylamine being formed, for example, in good yield from magnesium

phenyl bromide (Sand and Singer, *Ber.*, 1902, xxxv., 3186; *Annalen*, 1903, cccxxix., 190):—

$$NO \rightarrow O{:}N{.}N{:}O \rightarrow O{:}N{.}N{<}\begin{matrix}OMgBr\\C_6H_5\end{matrix} \rightarrow O{:}N{.}N{<}\begin{matrix}OH\\C_6H_5\end{matrix}.$$

Since carbon dioxide and sulphur dioxide form carboxylic and sulphinic acids respectively with a Grignard reagent, Wieland (*Ber.*, 1903, xxxvi., 2315) tried the action of nitrogen peroxide in the expectation of obtaining acids of the type R.NOOH. Instead of this type, however, he obtained, in the aliphatic series, *ββ*-dialkylated hydroxylamines, $R_2N.OH$, the nitrogen peroxide undergoing reduction. The preparation of *ββ*-diethylhydroxylamine is described. Negative results were obtained in the aromatic series (Wieland and Gambarjan, *Ber.*, 1906, xxxix., 1499).

The action of magnesium phenyl bromide on *β*-phenylhydroxylamine has been investigated by Busch and Hobein (*Ber.*, 1907, xl., 2099), who obtain a 20 per cent yield of triphenylhydrazine. Possibly azobenzene is formed as an intermediate product, and then interacts thus:—

$$C_6H_5.N{:}N.C_6H_5 + C_6H_5MgBr = \begin{matrix}C_6H_5\\C_6H_5\end{matrix}{>}N-N{<}\begin{matrix}C_6H_5\\MgBr\end{matrix}.$$

An alternative explanation is suggested as more probable. Phenylhydroxylamine is partially converted into diphenylamine, which then condenses with phenylhydroxylamine: $(C_6H_5)_2NH + OH.NHC_6H_5 = (C_6H_5)_2N.NHC_6H_5 + H_2O$.

It might be noted here that magnesium organic compounds sometimes exhibit a reducing action. Franzen and Deibel (*Ber.*, 1905, xxxviii., 2716), for example, show that hydrazobenzene may be obtained in good yield from azobenzene and magnesium ethyl bromide:—

$$\begin{matrix}C_6H_5.N\\ \|\\ C_6H_5.N\end{matrix} + 2Mg\begin{matrix}C_2H_5\\ \diagup\\ \diagdown\\ Br\end{matrix} = \begin{matrix}C_6H_5.N.MgBr\\ |\\ C_6H_5.N.MgBr\end{matrix} + C_4H_{10}$$

$$\begin{matrix}C_6H_5.N.MgBr\\ |\\ C_6H_5.N.MgBr\end{matrix} + 2H_2O = \begin{matrix}C_6H_5.NH\\ |\\ C_6H_5.NH\end{matrix} + 2MgBr(OH).$$

The action of the Grignard reagent on nitro-compounds has not been very thoroughly investigated. Moureu (*Comptes Rendus*, 1901, cxxxii., 837) obtained diethylhydroxylamine by the action of magnesium ethyl iodide on nitroethane and amylnitrite respectively. One of the products resulting from the action of magnesium ethyl iodide on nitrobenzene is ethyl aniline (Oddo, *Atti R. Accad. Lincei*, 1904, [5], xiii., II., 220).

A method of obtaining secondary amines from alkylidene bases is described by Busch (*Ber.*, 1904, xxxvii., 2691; compare Busch and Rinck, *Ber.*, 1905 xxxviii., 1761); thus C-methyl benzylaniline is obtained from magnesium methyl iodide and benzylidene aniline:—

$$C_6H_5.N{:}CH.C_6H_5 + MgCH_3I = C_6H_5.N\text{——}\begin{matrix}CH.C_6H_5\\ |\\ MgI\end{matrix}\begin{matrix}\\ |\\ CH_3\end{matrix}$$

$$C_6H_5.N\text{——}\begin{matrix}CH.C_6H_5\\ |\\ MgI\end{matrix}\begin{matrix}\\ |\\ CH_3\end{matrix} + H_2O =$$

$$= C_6H_5NH.CH(CH_3).C_6H_5 + MgIOH.$$

The action on oximes has been studied by Busch and Hobein (*Ber.*, 1907, xl., 2096), and takes place in accordance with the scheme—

$$R.CH{:}N.OH + 2R'MgX = \begin{matrix}R\\R'\end{matrix}{>}CH.N{<}\begin{matrix}R'\\MgX\end{matrix} + Mg{<}\begin{matrix}OH\\X\end{matrix}$$

$$\begin{matrix}R\\R'\end{matrix}{>}CH.N{<}\begin{matrix}R'\\MgX\end{matrix} + H_2O = \begin{matrix}R\\R'\end{matrix}{>}CH.NHR' + Mg{<}\begin{matrix}OH\\X\end{matrix}.$$

According to F. and L. Sachs, tertiary amines combine with magnesium organic compounds to form compounds which are insoluble in ether (*Ber.*, 1904, xxxvii., 3088; compare Oddo, *Atti R. Accad. Lincei*, 1904, [5], xiii., I., 100). The compound of quinoline and magnesium phenyl bromide is represented as $C_9H_7N.(MgBr)C_6H_5$.

Forster and Judd (*Trans. Chem. Soc.*, 1905, lxxxvii., 368), in studying the action of magnesium methyl iodide on *α*-cyanocamphor, found that about 80 per cent of the latter compound escaped attack by the reagent, whilst the remainder was converted into the imine

$$C_8H_{14}\begin{matrix}CH.C(CH_3){:}NH\\ |\\ CO\end{matrix}$$

, which on hydrolysis gave acetylcamphor.

When normal ethyl carbonate is added to the magnesium compound of a primary aromatic amine, one obtains a monosubstituted urethane, thus:—

$$2C_6H_5NHMgI + CO(OC_2H_5)_2 =$$

$$= (C_6H_5.NH)_2C(OC_2H_5).OMgI + MgI(OC_2H_5)$$

$$(C_6H_5.NH)_2C(OC_2H_5).OMgI + H_2O =$$

$$= C_6H_5NH_2 + C_6H_5NH.COOC_2H_5.$$

(Bodroux, *Comptes Rendus*, 1905, clx., 1108).

The application of the Grignard reagent for the preparation of diazoamino-compounds have been the subject of a series of papers by Dimroth (*Ber.*, 1903, xxxvi., 909; 1905, xxxviii., 670; 1906, xxxix., 3905). These compounds are obtained from diazobenzeneimide according to the scheme—

$$C_6H_5.N\begin{matrix}N\\ \|\\ N\end{matrix} + RMgX = C_6H_5.N(MgX).N{:}NR$$

$$C_6H_5.N(MgX).N{:}NR + H_2O = C_6H_5.NH.N{:}NR + MgXOH.$$

The method is particularly useful for the preparation of aliphatic or mixed aliphatic-aromatic diazoamino-compounds, for the preparation of which the older method of Griess is not available. Thus, phenylmethyltriazene, $CH_3.N_3H.C_6H_5$; benzylmethyltriazene, $CH_3.N_3H.CH_2C_6H_5$, &c., have been prepared. Diazoaminomethane, $CH_3.N{:}N.NH.CH_3$, was prepared from methylazide, $CH_3.N\begin{matrix}N\\ \|\\ N\end{matrix}$, and magnesium methyl iodide, according to the scheme given above. The isolation of this interesting compound was accompanied with great difficulties, due, on the one hand, to its instability, and, on the other, to the ease with which it dissolves in all solvents tried.

Alkyl and Aryl Metallic Compounds.

Pfeiffer and Schnurmann (*Ber.*, 1904, xxxvii., 319, 1125, 4617, 4618, &c.) describe a method of preparing alkyl and aryl metallic compounds by interaction of metallic halides, and the Grignard reagent either at the ordinary temperature or at 100°. Tin tetraethyl, for example, is prepared from tin tetrabromide and magnesium ethyl bromide: $SnBr_4 + 4C_2H_5MgBr = Sn(C_2H_5)_4 + 4MgBr_2$. Other tin compounds, such as tin tetraphenyl, tin tribenzyl chloride, tin trimethyl iodide, &c., are also obtained by this method, which has also been applied for making lead compounds; for example, lead tetraphenyl is obtained from lead chloride: $2PbCl_2 + 4C_6H_5MgBr = Pb + Pb(C_6H_5)_4 + 4MgClBr$.

The method has been very extensively applied, more particularly by Pfeiffer, for the preparation of derivatives of other elements such as mercury, thallium, phosphorus, arsenic, antimony, bismuth, and platinum.

Kipping (*Trans. Chem. Soc.*, 1907, xci., 209, 717) has made a special study of silicon compounds, and by aid of the Grignard reaction has prepared *dl*-sulphobenzylethylpropyl silicyl oxide,—

$$SO_3H.C_6H_4.CH_2.\begin{matrix}C_2H_5\\ |\\ Si\\ |\\ C_3H_7\end{matrix}-O-\begin{matrix}C_2H_5\\ |\\ Si\\ |\\ C_3H_7\end{matrix}.CH_2.C_6H_4.SO_3H,$$

and obtained evidence of the resolution of this compound into optically active components. Incidental to this work a number of silicon compounds are described, such as phenylethylsilicon dichloride, $C_2H_5(C_6H_5)SiCl_2$; phenylethylpropylsilicyl chloride, $C_2H_5(C_3H_7)(C_6H_5)SiCl$; phenylbenzylethylpropylsilicane, $C_2H_5(C_3H_7)(C_6H_5)(C_7H_7)Si$; benzylethylsilicon dichloride, $C_2H_5(C_7H_7)SiCl_2$; benzylethylpropylsilicyl chloride, $C_7H_7(C_2H_5)(C_3H_7)SiCl$, &c.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF POTASSIUM.*

II. The Analysis of Potassic Bromide.

By THEODORE WM. RICHARDS and EDWARD MUELLER.

(Concluded from p. 159).

The Drying and Weighing of Potassic Bromide.

For reasons already mentioned in the paper on potassic chloride, the salt under investigation must be fused before weighing. Unfortunately, potassic bromide when fused in air in a platinum vessel attacks the platinum to a considerable extent. Although it is shown later that this action does not seriously affect the weight of silver needed to precipitate the bromine in the salt, it was, nevertheless, desirable to avoid all such irregularities. No such action is observed when the fusion takes place in an atmosphere of pure dry nitrogen. Accordingly, in all work to be recounted, the potassic bromide was protected in this way during its fusion in a well-seasoned platinum boat, and was finally, by means of the Harvard "bottling apparatus," shut up in a tight weighing bottle in an atmosphere of pure dry air. The details have already been adequately given in several places, especially in the account of the recent work on the atomic weight of cæsium (Richards and Archibald, *Proc. Amer. Acad.*, 1903, xxxviii., 451; *Zeit. Anorg. Chem.*, 1903, xxxiv., 362). The only difference in the present procedure was demanded by the high fusing-point of potassic bromide (750°); on account of this, a porcelain ignition-tube was substituted for one of glass, as in the case of calcic chloride (Richards, *Journ. Am. Chem. Soc.*, 1902, xxiv., 374).

Even with all possible care, however, the platinum boat was distinctly attacked, almost always losing in weight during the fusion. In two of the cases—Analyses 1 and 14—where the potassic bromide was fused for some time in the boat, the corrosive action was very considerable, causing losses of weight of 0·0007 and 0·0014 grm. respectively. One would be disposed to reject these determinations entirely, except for the fact that their average result, $\frac{KBr}{Ag} = 1{\cdot}10317$, is almost exactly identical with that of the average of Results 5 and 6, in which the boat was scarcely attacked at all, namely, $\frac{KBr}{Ag} = 1{\cdot}10318$. Instead of being rejected, these results are therefore retained and used as evidence that even a considerable amount of dissolved platinum has no preceptible effect on the weight of silver precipitated by the salt. In a majority of the other cases, the change in weight of the boat during the fusion was less than 0·0001 grm. The average loss in Analyses 10, 11, 12, and 16, in which the argentic bromide was weighed, was less than 0·00009 grm.; hence, even if platinum had been present in the potassic bromide in a state of fine division it could not have exerted any essential effect upon the result of this series of analyses.

As a matter of fact, the potassic bromide always gave a perfectly clear aqueous solution except once, namely, in Analysis 14. In this case several small flakes of platinum were noticed in the salt both before and after the salt was dissolved in water.

The solutions were always perfectly neutral to phenolphthaleïn, a fact which is adequate proof of the retention of all the bromine during fusion, and also of the absence of oxalate from the potassic bromide crystals.

The third sample of potassic bromide had contained ammonic bromide, which was expelled during the fusion. During the expulsion of this salt, the boat was placed near the exit end of the porcelain tube, and there gradually heated to redness in a current of nitrogen. During the entire operation the middle portion of the porcelain tube was kept red-hot in order to prevent backward diffusion of the ammonic bromide, which by condensing might later cause a contamination of the potassic bromide. All the ammonic bromide having been sublimed, the boat was pushed into the middle of the tube, and the potassic bromide fused as described above. There being a possibility that even at the fusing-point of potassic bromide some ammonic bromide might still be retained, another portion of the same third sample of bromide was fused under approximately the same conditions as in the analyses. The solution of the bromide thus obtained was submitted to the Nessler test, being compared with a tube of pure water containing the same amount of reagent. No colour was visible in either tube, hence no appreciable amount of ammonic bromide remained to contaminate the potassium salt.

The salt thus prepared for analysis was weighed in its glass-stoppered weighing bottle by substitution, using as the substituting tare a precisely similar weighing bottle. Successive weighings of the same specimen were always practically identical. The balance and weights were similar to those used with sodic and potassic chlorides, and all the precautions were the same. At each weighing the heights of the barometer, the temperature of the balance-room, and the humidity as indicated by a hygrometer were recorded. The density of the displaced air could thus be determined for each case. The variations from the average were, however, not enough to affect essentially any of the results, as weighings were not made under any abnormal atmospheric conditions. The weights were of course standardised by the usual Harvard method.

The specific gravity of potassic bromide must be known to within five one-hundredths of a unit in order to correct the weighings to the vacuum standard with sufficient accuracy. Its determination has been undertaken with a variety of methods, with a variety of results, ranging from 2·20 to 2·756. (For the literature, see Meyerhoffer, "Landolt u. Börnstein"; "Physikalisch-Chemische Tabellen," 1905; and Clarke, "Constants of Nature," Part I., Macmillan, 1888). The more recent results all tend towards the highest value, found by Krichmeyer, 2·756 (*Zeit. Physikal. Chem.*, 1896, xxi., 81). This appeared to be the most probable, because the usual errors cause low results; but as this determination was made with only a single crystal, and as the salt weighed in the present research had been fused, it was thought best to investigate further. Accordingly, a pure sample of potassic bromide was further purified by being three times recrystallised with centrifugal draining, when it gave no flame test for sodium (see Krichmeyer's experience, *loc. cit.*). This product was fused in platinum and coarsely pulverised; its specific gravity was determined in an Ostwald pycnometer, modified for use with solids, using toluol as the fluid to be displaced. The toluol had been re-distilled, and possessed a density 0·8608 at 25°, referred to water at 4°; 8·2568 grms. of potassic bromide displaced 2·6009 grms. of the toluol at 25°, a result which indicates a density of 2·73. Time was lacking for a repetition of the experiment, but this preliminary result was enough to show that the fused salt is essentially in the same state as the crystallised salt. The difference between the two values is too small to affect the vacuum correction; the average value 2·74 was used.

The Precipitation and Weighing of Argentic Bromide.

In order to determine the weight of argentic bromide obtainable from the bromine in potassic bromide, the latter salt was precipitated by a very slight excess of argentic nitrate, both substances being dissolved in large quantities of the purest water. The method differed but slightly from that which had been used recently in so many other cases of the same kind. The argentic nitrate was prepared from a weighed amount of pure silver, but no attempt was made in this series to determine the exact amount of silver required, as it was desired not to complicate the process before weighing the argentic bromide. Care was taken to have an excess, but only a slight excess. The silver was dissolved in nitric acid with

* *Publication* No. 69, Carnegie Institution of Washington.

all the usual precautions, and the precipitation was carried out in orange-red light in the dark-room devoted to accurate work of this kind. The potassic bromide had been dissolved out of the boat by digestion in a large platinum dish, and been transferred to a 2 litre glass-stoppered Jena Erlenmeyer flask with careful rinsing, and every precaution to prevent any gain or loss. After being well shaken, the flask containing the silver bromide was allowed to stand until the mother-liquor had become clear. The solution was filtered through a platinum Gooch-Munroe crucible, and the precipitate was washed by decantation, first with an extremely dilute acid solution of silver nitrate, and finally with exceedingly dilute nitric acid to prevent colloidal solution. With this latter faintly acid liquid the precipitate was transferred to the crucible. The silver bromide was dried at least twelve hours in the filtering crucible at 130° in an electric oven, and weighed (Richards, *Am. Chem. Journ.*, 1899, xxii., 45). It was then fused in a porcelain crucible, in a furnace where it was effectively protected from flame gases, in order to determine the trace of moisture always retained. The wash-waters and the solution obtained on neutralising the ammoniacal rinsings of the flask gave no indication of the presence of bromine on careful testing in the nephelometer.

In using the Gooch-Munroe crucible, all the precautions pointed out in the preceding paper were carefully heeded. A perforated plate was always placed on top of the friable sponge to prevent rupture. After each determination any bromide clinging to it was leached out with potassic cyanide, which was then washed away with nitric acid, and finally very thoroughly with water. The solvent action of the cyanide occasionally loosened portions of the spongy film, but there was no difficulty in repairing the injury. Upon drying in the electric oven, the crucible was ready for another analysis.

In addition to the loss of weight on fusion, two other very small and somewhat uncertain corrections were applied to the weight of the argentic bromide, but because they were of about the same magnitude and of opposite sign, their effect was practically negligible. These were a correction for platinum corroded from the boat during the fusion of potassic bromide, and a correction for argentic bromide dissolved in the water used for washing. Because these corrections have not been considered in most work of this kind, a word about them may not be amiss.

In the series under discussion the average loss of the boat in each determination was less than 0·00009 grm. All of this trace of platinum may have been present as invisible dust in the solution, and thus may have been weighed with the argentic bromide, or all of it may have been in a soluble form and may have remained in solution. Because of this uncertainty, a compromise was made, and half of the loss of weight of the boat (in the mean 0·00004 grm.) was subtracted from each weight of argentic bromide. As the average total weight of argentic bromide was over 4 grms., this compromise could not have introduced an error as great as 1 part in 100,000 in either direction.

According to Stas (" Œuvres," I., 89), argentic bromide is wholly insoluble in water, but recent experiments show that in the flocculent form it is unquestionably soluble to a slight extent (Böttger, *Zeit. Phys. Chem.*, 1903, xlvi., 602; Kohlrausch and Rose, *Zeit. Phys. Chem.*, 1893, 12, 234; also Richards, *Proc. Amer. Acad.*, 1894, xxx., 385). As in the case of the chloride, its solubility is greatly diminished by the addition of an excess of either precipitant; but whether or not any is dissolved by a very dilute acid solution of argentic nitrate, such as that used in washing, it is practically impossible to discover. It is not unlikely, however, that about as much was dissolved by this solution as by the dilute hydrobromic acid used by Baxter in his admirable work on the atomic weight of bromine (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1322); and in this solution it is easy to find the amount of dissolved substance. Baxter found, as a matter of fact, in his last seven most exact syntheses an average of 0·00004 grm. of argentic bromide in each of the wash-waters—a figure which was added to each of our weights of argentic bromide, because the other circumstances of the analysis were similar in the two cases. On the average, this correction exactly eliminates the other, and except for the sake of completeness, they might both have been wholly neglected.

Of course, all the weighings were corrected to the vacuum standard, by adding 0·00041 grm. to every apparent grm. of argentic bromide and 0·00029 grm. to every apparent grm. of potassic bromide, as calculated from the figures 6·473, 2·74, and 8·30, for the densities of argentic bromide (Baxter and Hines, *Am. Chem. Journ.*, 1904, xxxi., 220), potassic bromide, and the brass weights respectively. All the determinations made are given in the table below.

The Ratio of Argentic Bromide to Potassic Bromide.

Experiment No.	Weight of KBr in vacuum. Grms.	Corrected wt. of AgBr in vacuum. Grms.	Parts of KBr for 100·00 parts of AgBr.	At. wt. of potassium Br = 79·953.
10.	2·19027	3·45617	63·3728	39·114
11.	4·19705	6·62285	63·3723	39·113
12.	2·06723	3·26206	63·3719	39·112
16.	2·58494	4·07889	63·3736	39·115
Total average	11·0395	17·41997	63·3727	39·1135
Probable error			0·0003	0·0004

The extreme deviation from the mean corresponds to an error of weighing the potassic bromide of 0·00004 grm., a reasonable quantity. The " probable error " indicates that there is but little chance that the atomic weight of potassium is much below 39·113 or much above 39·114, if constant chemical errors were successfully excluded. Stas found in a single experiment the number 63·383 instead of 63·373 (" Untersuchungen," *Trans. Aronstein*, 1867, p. 340).

With unlimited time more determinations might well have been made, but the agreement of these four results is so good that further repetition seemed to be not very urgent.

The Determination of the Silver needed for Precipitation.

The silver titration method of Guy-Lussac, as developed by Pelouze, Mulder, Stas, and more especially by the recent work at Harvard, yields very consistent and accurate results, if the proper conditions are carefully observed. The reading of the end-point is rendered easy by the use of the nephelometer (Richards and Wells, *Am. Chem. Journ.* 1904, xxxi., 235). In the case of the somewhat soluble chloride, various precautions must be strictly heeded; but with argentic bromide, which is almost insoluble, the matter is a simpler one, and a very slight excess of either bromide or silver can be easily determined.

The method used in the present case is easily inferred from previous Harvard work of the same kind. From the weight of a piece of the purest silver, the equivalent amount of potassic bromide was calculated; slightly more than this amount of substance was then fused as before in a platinum-iridium boat placed in the porcelain tube of the bottling apparatus. From the weight of fused bromide, the equivalent quantity of silver was calculated; the greater part of the difference between this calculated weight and that of the original piece of silver was added in the shape of pure silver wire (Richards and Parker, *Proc. Amer. Acad.*, 1896, xxxii., 60), and any final difference of 0·1 or 0·2 mgrm. was made up with a dilute solution of silver nitrate. The silver was dissolved in nitric acid, and the nitrous acid expelled as usual, and the solution was then diluted to about tenth normal.

To the dilute bromide solution, with continual agitation, was added this dilute argentic solution; the total volume, including the water used in rinsing, usually amounted to about 1·5 litres. After shaking steadily for fifteen minutes, and occasionally for a day, the mixture was allowed to

settle during another day. When clear above, about 0·05 litre of the aqueous solution was withdrawn and tested in the nephelometer, one tube being treated with an excess of bromide, the other with an excess of argentic nitrate. If any difference in the opalescence was noticeable after due time had been allowed for the very faint clouds to attain their maxima, the slight deficiency was made up in the flask by means of solutions containing approximately 1 mgrm. of argentic nitrate or of potassic bromide per millilitre. These additions were continued till equality in the opalescence was attained. From the sum of the original weights and subsequent additions, the total amounts of bromide and silver were obtained; from these, reduced to vacuum, the ratio was calculated. All the analyses which were performed are given in the table, excepting No. 2, which was rejected for just cause before it was finished. Vacuum corrections of +0·00029 for every grm. of potassic bromide and −0·00003 for every apparent grm. of silver were applied. Most of these experiments were made before those given in the preceding table, a fact which may account for the slightly less satisfactory agreement of the individual results. Because the deviations could not be traced to any definite cause of disturbance, they must be ascribed to accident.

The Ratio of Potassic Bromide to Silver.

Experiment No.	Weight of KBr in vacuum. Grms.	Weight of silver in vacuum. Grms.	Parts of KBr corresponding to 100·00 parts Ag.	Atomic weight of potassium if Br=79·953.
1.	4·33730	3·93164	110·318	39·113
3.	4·18763	3·79587	110·320	39·115
4.	4·15849	3·76943	110·321	39·116
5.	3·67867	3·33450	110·321	39·116
6.	3·60484	3·26776	110·315	39·110
7.	4·78120	4·33387	110·322	39·118
8.	5·67997	5·14860	110·321	39·116
9.	6·41587	5·81571	110·320	39·115
13.	2·88134	2·61184	110·318	39·113
14.	3·64383	3·30309	110·316	39·111
15.	3·12757	2·83504	110·318	39·113
	Total average		110·3190	(*a*) 39·1143
	Probable error		0·0004	0·0004

(*a*) The average 39·1143 is calculated from the average 110·3190, not from the average of the individual values of the atomic weights in the column above. The difference of course is very slight.

The "probable error" is as small as before because of the greater number of determinations, and the mean deviation from the average value is only one in the last decimal place. It will be observed that these results point to the limits 39·113 and 39·115 as the extreme values between which the atomic weight of potassium must fall, in essential agreement with the previous results.

Marignac's seven experiments on this ratio give values ranging from 110·303 to 110·369, while Stas's fourteen results ranged from 110·332 to 110·361.

Obviously the results furnish a means of calculating the atomic weight of bromine, when taken in connection with the foregoing series, entirely independent of any other work. Thus, Br = (110·319/63·3727—1·00000) 107·93 = 79·954, a value almost identical with Baxter's value, 79·953. This is excellent proof that the bromine used in the present research was pure, and that the occlusion of electrolytes by argentic bromide was small.

The Atomic Weight of Potassium.

The preceding paper and the present one together yield four ratios determined with modern precision, which together fix the atomic weight of potassium as definitely as could be expected. The respective values are as follows:—

	K=
From the ratio of argentic to potassic chloride	39·1134
From the ratio of metallic silver to potassic chloride	39·1145
From the ratio of argentic to potassic bromide	39·1135
From the ratio of metallic silver to potassic bromide	39·1143
Average atomic weight of potassium if Ag = 107·930	39·1139

These figures are interesting and significant. The maximum departure from the mean is only 1 part in 70,000, and such differences as exist in the figures are explicable. It is likely that the slightly lower value given by the first member of each pair of series was due to a trace of occlusion of potassic nitrate by each of the precipitates—a circumstance which cannot be absolutely prevented. Therefore the higher values, averaging 39·1144, are more probable. The differences are, however, wholly negligible at present.

In this connection it is interesting to note that Clarke in 1897, from a miscellaneous collection of partly uncertain results obtained by others, decided upon the almost identical value, 39·112 ("Re-calculations," p. 57), although at the same time from similar results he obtained values much too low for chlorine and iodine, somewhat too low for bromine, and much too high for sodium.

The very close mutual agreement of the new results obtained from two different compounds is a satisfactory verification of the relative values yielded by the recent work on the atomic weights of chlorine and bromine (Richards and Wells, *loc. cit.*; Richards, *Trans. Am. Phil. Soc.*, 1904, xliii., 116; Baxter, *loc. cit.*). The value of chlorine found from the work on potassium chloride was 35·475, and that of bromine from the present work is 79·954. The ratio of chlorine to bromine is thus found to be 0·44369, whereas the ratio computed from the work of Richards and Wells, and of Baxter, is 0·44367.

Against such an accumulation of concordant data as that just presented, the older figures can have no important weight. Whatever may have been the cause of the irregularity and internal inconsistency of Stas's results with potassic chloride and bromide, there seems to be little reason to doubt that the outcome of the present investigation, 39·114, really represents the atomic weight of potassium.

It is needless to point out that this change in the atomic weight of potassium will affect many other atomic weights.

Summary.

This investigation upon the atomic weight of potassium presents, among other considerations, the following additions to the knowledge of the subject:—

1. The problem of preparing pure potassic bromide was solved in two ways.

2. An unusually satisfactory method for preparing pure potassium hydroxide was developed. This method is applicable to other alkalis, and will be described elsewhere in greater detail.

3. The ratio of silver to potassic bromide was re-determined, and found to be 100·000 : 110·319. The atomic weight of potassium was thus found to be 39·1143, if silver is 107·930 and bromine 79·953.

4. The ratio of argentic bromide to potassic bromide was found to be 100·000 : 63·373. This determination yielded an essentially equal value, K = 39·1135.

5. These values confirm in a striking manner the simultaneously executed work upon potassic chloride, and unite with them in showing that the atomic weight of potassium is 39·114.

6. By thus agreeing, these four values support the new value for the atomic weight of chlorine in relation to silver and bromine.

Radio-activity of Uranyl Molybdate.—B. Szilard.—The author has prepared uranyl molybdate by the same process as Lancien, in order to examine the truth of the latter's statement as to its abnormally high activity. He finds, however, that the radio-activity is absolutely normal and proportional to the amount of uranium present.—*Comptes Rendus*, cxlv., No. 10.

NOTICES OF BOOKS.

The Principles and Practice of Brewing. By Walter J. Sykes, M.D., D.P.H., F.I.C. Third Edition, thoroughly Revised by the Author and Arthur R. Ling, F.I.C. London: Charles Griffin and Co., Ltd. 1907.

This valuable treatise combines a text-book of the theory of brewing, dealing with the physics, chemistry, and biology of the subject, with a practical laboratory guide in which a systematic course of the experimental work necessary for a thorough study of brewing and malting is given. It is clearly and authoritatively written, and no better recommendation can be urged than the fact that it has reached its third edition in less than ten years. The text had been revised, with the co-operation of Mr. Ling, by Dr. Sykes before his death in December last year, and the work has been brought thoroughly up-to-date; the new edition contains important additions on thesubject of stereochemistry, and the chemistry of the carbohydrates and the enzymes, while other parts of the book have also been considerably enlarged.

Recent Improvements in Methods for the Biological Treatment of Sewage. By W. J. Dibdin, F.I.C., F.C.S. Second Edition. London: Sanitary Publishing Company.

This book contains a description of the author's Multiple Surface Biological Beds, for dealing with suspended matters with aërobic action throughout, which have been used in different localities with exceedingly satisfactory results, and it further gives a condensed account of modern methods of sewage treatment. It treats more especially of biological processes in which no chemical agents are employed, and the statistics quoted show that the double contact bed system, with slate as the filling for the primary beds, is not to be surpassed for simplicity and economy. The book may be regarded as a supplement to the third edition of the author's well-known treatise on "The Purification of Sewage and Water," giving details of researches and experiments performed since its publication.

The Dispensatory of the United States of America. By Dr. Geo. B. Wood and Dr. Franklin Bache. Nineteenth Edition. by H. C. Wood, M.D., LL.D., Joseph P. Remington, Ph.M., F.C.S., and Samuel P. Sadtler, Ph.D., LL.D. Philadelphia and London: J. B. Lippincott Company.

The Food and Drugs Act, with Rules and Regulations, of the United States Government is printed in full in this Dispensatory, which will be found invaluable by druggists and pharmacists. An abstract of the national formulary is included, and as in the earlier editions the official and unofficial preparations both of the United States and British Pharmacopœias are separated. In Part III. the tests and test solutions for determining the purity and strength of many important chemicals are given, and fuller references are now added to chemical, pharmaceutical, and therapeutical literature. Thus the Nineteenth Edition represents a decided advance upon the earlier volumes of the Dispensatory, and it is clear that every endeavour has been made to render it fuller and more convenient in use than its predecessors.

The Electric Furnace in Iron and Steel Production. By John B. C. Kershaw, F.I.C. London: The Electrician Printing and Publishing Company, Ltd. 1907.

This book is based upon a series of papers contributed by the author to the *Iron Trade Review*, of Cleveland, U.S.A., last year, and afterwards published in *The Electrician*. In them the author considered in detail the four chief types of furnaces and processes—those of Heroult, Keller, Kjellin, and Stassano—which have been subjected to lengthy trials upon an industrial scale, and also discussed shortly some methods which have not been so long before the public, and which can hardly be said to have passed the experimental stage. Although it is undeniable that all electric smelting processes appear to be utterly unable to compete with blast-furnace processes at present, except possibly under peculiarly favourable combinations of circumstances, there seems to be much more likelihood that electric refining methods will begin to be widely used with financially satisfactory results, and the book gives a useful summary of the present state of affairs; the author has endeavoured to sift out from the great number of figures relating to yields and costs, which have appeared in various periodicals, those which are based upon actual experimental results and not upon estimated expenses, and the chapter upon this subject is well worth the careful consideration of engineers.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 9, August 26, 1907.

Propylene Oxide, $H_3C{-}CH{-}CH_2$ (O bridging CH and CH_2).—Louis Henry.—When an ethereal solution of propylene oxide acts upon ethyl magnesium bromide, also dissolved in ether, an alcoholic liquid is obtained boiling at 115—120°. This may be either $CH_3{-}CH(OH){-}CH_2{-}CH_2{-}CH_3$ (boiling-point 118°) or $CH_3{-}CH_2{-}CH(OH){-}CH_2{-}CH_3$ (boiling-point 116°). These two alcohols may be differentiated by converting them into semicarbazones. The semicarbazone of methyl propylketone, $H_3C{-}CH_2{-}CH_2{>}C=N{-}NH{-}CO(NH_2)$, fuses at 100°, while that of the symmetric diethyl ketone, $H_3C{-}CH_2{>}C=N{-}NH.CO(NH_2)$, fuses at 138°. By this method it may be shown that the alcohol is normal methyl propyl carbinol, $CH_3{-}CH(OH){-}CH_2{-}CH_2{-}CH_3$. Thus propylene oxide behaves towards magnesium derivatives in the same way as ethylene oxide.

No. 10, September 2, 1907.

Action of Gravity on the Deposit of Induced Radio-activity. — Mdme. Curie. — Some years ago, P. Curie observed that when radium emanation is contained in a closed vessel the interior of which is covered with phosphorescent zinc sulphide, the luminosity of this substance under the action of the emanation is gradually concentrated in the regions round the bottom. When the vessel is turned upside down, so that the luminous part is at the top, the luminosity of the upper part gradually disappears, while a new luminous region is formed below. The position of the region appears to be independent of the neighbourhood of magnets and of the temperature. The experiments of P. Curie and Debierne have shown that a metal sheet placed in a closed vessel which contains some emanation becomes more active the greater the free space in front of the sheet. When two parallel sheets are placed face to face, if their area is large compared with their distance apart, the activity acquired by the opposite faces increases with the distance. The author has placed in a vessel containing emanation pairs of parallel sheets, all at the same distance, some horizontal and others vertical, the exterior faces being protected, so that only the faces turned towards one another could become active. When the plates were exposed to the action of the emanation for two or three days, the emanation was drawn off and the intensity of the radio-activity of the active faces of different sheets determined. It was found that all the vertical sheets, and all the horizontal ones turned downwards, have the same activity for equal surfaces, while the horizontal sheets turned upwards have

an activity from two to five times as great. Hence the induced radio-activity suspended in the gas which surrounds the sheets behaves like a heavy substance, and falls downwards. The presence of water is necessary for the production of the phenomenon, and when the air in the vessel is quite dry the phenomenon does not occur. The intensity of the phenomenon seems to depend upon the concentration of the emanation. It depends also upon the distance of the sheets, and increases with it up to a certain limit. The phenomenon does not occur at very small distances (2 mm.).

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RESEARCHES ON THE DENSITIES OF GASES.

By PHILIPPE A. GUYE.

The researches described in this paper were carried out during the past three years in the Laboratory of Physical Chemistry of the University of Geneva, in collaboration with MM. Jaquerod, Pintza, Davila, Gazarian, and Baume. The aim of the experiments was to determine with as great a degree of accuracy as possible the molecular weights of the gases in order to provide a control for the atomic weights. Two methods of determining the densities were employed—Regnault's bulb method and the volumeter method. In the former, Regnault's directions were followed closely, small bulbs of capacities 0·8 and 0·4 litre being used. Contrary to expectation it was found that the results with small bulbs agreed amongst themselves quite as well as those obtained in experiments with much larger bulbs, probably because errors arising from accidental causes connected more especially with the surface were minimised. The only objection to the use of small bulbs is the fact that possibly condensation may occur on the inner wall, especially in the case of hygroscopic gases; it is essential to rinse the bulbs not only with air dried over phosphorus pentoxide, but also with the thoroughly dried gas which is being examined. Each operation must be followed by complete evacuation, and the air must not be allowed to enter the bulb between the determinations. The volumeter method, first employed by Morley to determine the density of hydrogen, may be carried out in two ways. The gas may be set free from an apparatus which can be weighed, and which is constructed in such a way that the gas can come out only in a perfectly pure dry state. The gas then passes into a series of one or more graduated bulbs kept at 0°, and exhausted by a mercury pump. The pressure is measured either with a special manometer or else by means of a barometer. Then, since the temperature, pressure, capacity of the bulbs, and loss of weight of the generating apparatus are known, the density can be calculated. In the second method the volumeter after being exhausted is filled with the gas in as pure a state as possible, and kept at 0° in ice; the exact pressure of the gas is noted. Then it is absorbed in an appropriate apparatus, previously weighed. The volumeter method does not need correction for the contraction of the bulbs; it is only necessary to reduce the weight found to the weight *in vacuo*, for a counterpoise made of the same glass and having the same weight as the generating or absorbing apparatus is used. Whatever method is employed the correction for the compressibility of the gas can generally be neglected, when the pressure differs from 760 mm. by only a few mm.

Choice of a Unit.—It is absolutely indispensable to choose a common unit, and it is found most convenient to express all the results in terms of the weight of the normal litre of the gas, *i.e.*, at 0° C., under a pressure of 760 mm., at sea level and in latitude 45°.

Choice of Definite Values.—When making a choice between different numbers obtained for the density of each gas, the following points have been taken into consideration:—1. The nature of the methods employed for preparing and purifying the gas. Concordant results obtained with the same gas prepared in two or three different ways are always regarded as the most reliable. 2. Degree of agreement of the mean values of the same gas as determined by different observers. When the mean values of two observers agree, but differ from that of a third, the latter is, generally speaking, ignored.

Discussion of the Results.

Oxygen.—Morley performed forty-one determinations of the density of oxygen under very different conditions; these give as the mean value of the weight of the normal litre 1·42900 grm. Rayleigh used oxygen prepared by three different methods, and obtained the number 1·42905 grms. Other results are given, with the experimenters' names, in the following table:—

	Grms.
Morley	1·42930
Rayleigh	1·42905
Gray	1·22896 (*a*)
Leduc	1·4288
Jaquerod and Pintza	1·4292
Mean	1·4290

(*a*) As printed; evidently should be 1·42896.—*Ed.* C.N.

Thus, the value 1·42900 grms. for the weight of the normal litre is certainly accurate to within 1/10000 and probably within 1 20000.

Nitric Oxide, NO.—Gray was the first to determine accurately the density of this gas. He prepared it by the action of acetic acid on sodium nitrite and potassium ferrocyanide; then washed with caustic potash, dried over phosphorus pentoxide, liquefied, and fractionated at a low temperature. The results obtained agreed remarkably well among themselves, and also with those of Guye and Davila, the mean value being 1·3402 grms.

Carbon Dioxide, CO_2.—The mean values of the results obtained by Rayleigh, Leduc, and Guye and Pintza are 1·9769, 1·9763, and 1·9768 respectively. The last is probably the most correct.

Nitrous Oxide, N_2O.—Leduc found 1·9780, using the commercial liquefied gas. Rayleigh in two separate series of experiments, using gas prepared by different methods, found 1·9777, while Guye and Pintza, obtaining the gas by the double decomposition of sodium nitrite and hydroxylamine sulphate, found 1·9774. Taking into account the fact that possibly by the last method the gas is not obtained absolutely free from air, it appears probable that the last number is low, and the value adopted is Rayleigh's, viz., 1·9777, which is also the mean of Leduc's, Guye and Pintza's, and Rayleigh's.

Hydrochloric Acid, HCl.—The mean of numbers obtained by Guye and Gazarian, and Gray, is 1·6398, which may be adopted provisionally; new determinations are, however, being carried out.

Ammonia, NH_3.—Leduc found 0·7719 grm., which, however, must be rejected because it is affected by an error due to the presence of organic bases. Guye and Pintza obtained 0·7708, and Perman and Davies 0·77085. The former may be accepted as correct.

Sulphurous Anhydride, SO_2.—The value 2·9266 has been found by Jaquerod and Pintza, Leduc and Baume.

The accompanying table gives a summary of these results. Column I. gives the values found by Leduc, Column II. those of Rayleigh, In Column III. the results of different observers are given (Morley, Ramsay, Gray, Perman, and Davies), and in Column IV. the figures obtained in the author's laboratory in Geneva. Column V. gives those numbers which in the author's opinion are probably correct, and in Column VI. the ratios to the densities of oxygen are tabulated.

The following general conclusions can be drawn from the work carried out in the author's laboratory in Geneva during the last three years:—

1. Methods of determining the densities of gases in the hands of different experimenters give results which agree generally to within 1/10,000 at least, when the mean of six experiments, which do not differ among themselves by more than 3/10,000 or even 5/10,000, is taken.

2. This agreement can be obtained with gases which are very difficult to dry and purify, such as ammonia, sulphurous anhydride, hydrochloric acid, and nitric oxide. The bulbs must be thoroughly dried with dry air, and then

Weight of Normal Litre, in Grms. ($t=0°$, $H=760$, $h=0$, $\lambda=45°$).

Gas.	I. Leduc.	II. Rayleigh.	III. (Various).	IV. Guye's laboratory.	V. Values accepted.	VI. Densities referred to O_2.
O_2	(1·4288)	1·42905	{ 1·42900 M. 1·42896 Gr.	(1·4292) J. P.	1·42900	1·00000
H_2	0·8982	(0·08998)	0·0898873 M.		0·08987	0·062890
N_2	1·2503	1·2507	1·2507 Gr.		1·2507	0·87523
CO	1·2501	1·2504			1·2504	0·87502
NO	(1·3429)		1·3402 Gr.	1·3402 G. D.	1·3402	0·93786
Ar		1·7809	1·7808 R.			1·2463
CO_2	1·9763	1·9769		1·9789 G. P.	1·9768	1·3833
N_2O	1·9780	1·9777		1·9774 G. P.	1·9777	1·5840 (*a*)
HCl	(1·6407)		1·6397 Gr.	1·6398 G. G.	1·6398	1·1475
NH_3	(0·7719)		0·77085 P. D.	0·7708 G. P.	0·7708	0·53940
SO_2	2·9266			{ 2·9266 J. P. 2·9266 B.	2·9266	2·0480
Air	1·2927	1·2928			1·2928	0·90469

(*a*) As printed; evidently should be 1·3840.—*Ed.* C.N.

rinsed with the perfectly dry gas. If this is done, no appreciable differences are found between the values obtained with 3·5 litre bulbs and with those holding only 0·5 litre.

3. The experimenter must pay special attention to the purification of the gas. Processes based upon the liquefaction of the gas, followed by rectification at low temperatures, are specially recommended.

4. It is preferable to calculate directly the weight of the normal litre of the gas, rather than to refer the densities to those of a standard gas, *e.g.*, oxygen or air.—Abstracted from the *Archives des Sciences Physiques et Naturelles*, xxiv., p. 34.

OBSERVATIONS AND DEDUCTIONS OBTAINED FROM A CONSIDERATION OF THE NUMBERS GIVEN FOR THE ATOMIC WEIGHTS OF THE ELEMENTS BY THE INTERNATIONAL COMMITTEE (1905) WHICH LEAD TO A RATIONAL DETERMINATION OF THE CONSTITUTION AND STRUCTURE OF EACH ELEMENT.

By HAWKSWORTH COLLINS, B.A. (Camb.).

1. THE first observation, which is not original, was made several years ago, viz., that the numbers obtained for the atomic weights of many elements approximate to whole numbers. In an investigation with regard to the constitution and structure of elements, this observation is too patent to be ignored.

(A). The first deduction, which is of course, not original, is that the elements are multiples of the element hydrogen.

2. The second observation is entirely original, as are all the others in this paper. It is that "artiads" have even atomic weights and "perissads" have odd atomic weights, with the single exception of nitrogen. That is, those elements which have even valencies have even atomic weights, and those elements which have odd valencies have odd atomic weights, with the exception of nitrogen.

This observation only applies to elements of less atomic weight than 63, because after this the difference between the two series of atomic weights is greater than 0·5, and it is impossible to decide whether the atomic weight approximates to an even or an odd whole number.

The atomic weights of the twenty-eight elements concerned in this investigation are now given as determined by the International Committee on Atomic Weights (1905). (See Table I.).

TABLE I.

Element.	Symbol.	O=16.	H=1.	Obvious whole number.
Hydrogen ..	H	1·008	1·000	1
Helium ..	He	4	4	4
Lithium ..	Li	7·03	6·98	7
Glucinum ..	Gl (Be)	9·1	9·03	9
Boron	B	11·0	10·9	11
Carbon . ..	C	12·0	11·91	12
Nitrogen ..	N	14·04	13·93	14
Oxygen . ..	O	16·00	15·88	16
Fluorine ..	F	19	18·9	19
Neon	Ne	20	19·9	20
Sodium ..	Na	23·05	22·88	23
Magnesium .	Mg	24·38	24·18	24
Aluminium .	Al	27·1	26·9	27
Silicon . ..	Si	28·4	28·2	28
Phosphorus .	P	31·0	30·77	31
Sulphur ..	S	32·06	31·82	32
Chlorine ..	Cl	35·45	35·18	35
Potassium ..	K	39·15	38·85	39
Argon	A	39·9	39·6	40
Calcium ..	Ca	40·1	39·7	40
Scandium ..	Sc	44·1	43·8	44
Titanium ..	Ti	48·1	47·7	48
Vanadium ..	V	51·2	50·8	51
Chromium ..	Cr	52·1	51·7	52
Manganese .	Mn	55·0	54·6	55
Iron	Fe	55·9	55·5	56
Cobalt . ..	Co	59·0	58·55	59
Nickel	Ni	58·7	58·3	59

3. The third observation is that all the numbers under O = 16 are either equal to whole numbers or *greater than* whole numbers, except A, Fe, and Ni. The property of magnetism in the two latter elements may account for the slight diminution of atomic weight.

(B). The second deduction is that the increase in the atomic weights of elements above whole numbers is due to the condensation of protyle within each atom, and that this condensation accounts for the observed emission under certain conditions of exceedingly small material particles from substances.

4. The fourth observation is that, in nine instances, a difference of 4 in the list of "obvious whole numbers" corresponds to a difference of two valencies. The nine instances are given in Table II.

Table II.

Li	Monad ..	7	4	Na	Monad ..	23	4
B	Triad ..	11		Al	Triad ..	27	
Mg	Dyad ..	24	4	Al	Triad ..	27	4
Si	Tetrad ..	28		P	Pentad ..	31	
Si	Tetrad ..	28	4	P	Pentad ..	31	4
S	Hexad ..	32		Cl	Heptad ..	35	
Ca	Dyad ..	40	4	Sc	Tetrad ..	44	4
Sc	Tetrad ..	44		Ti	Hexad ..	48	
V	Pentad ..	51	4				
Mn	Heptad ..	55					

5. The fifth observation is that in every case the above increment of 4 corresponds to an addition of two *acidic* forces; or, in other words, of two forces the nature of which has caused all elements containing them to be classed as non-metallic.

6. The sixth observation is that one of this pair of forces emanates from a portion of the element whose mass is 1, and the other from a portion of the element whose mass is 3. This is evident from Table III.

Table III.

B	Triad ..	11	1	Na	Monad .	23	1
C	Tetrad ..	12		Mg	Dyad ..	24	
Al	Triad ..	27	1	P	Pentad ..	31	1
Si	Tetrad ..	28		S	Hexad ..	32	
K	Monad ..	39	1	V	Pentad ..	51	1
Ca	Dyad ..	40		Cr	Hexad ..	52	
Mg	Dyad ..	24	3	Si	Tetrad ..	28	3
Al	Triad ..	27		P	Pentad ..	31	
S	Hexad ..	32	3	Cr	Hexad ..	52	3
Cl	Heptad ..	35		Mn	Heptad ..	55	

(C). The third deduction is that the acidity or non-metallic nature of an element is always due to a pair or pairs of electro-positive forces, each pair emanating from a portion of the element, of which the mass is 4, taking the mass of an atom of hydrogen as unity.

7. The seventh observation is that acidic forces always occur in pairs.

8. The eighth observation is that, if the values given for the atomic weights of certain elements be reduced in the ratio 35·45 : 35, these reduced values approximate to whole numbers. The elements referred to are Be, Mg, Si, and Cl. The atomic weights of the first three are especially dependent upon that of Cl. Bromine will also be considered in this observation, since its value is well known to be especially dependent upon that of Cl.

The atomic weights of these five elements, when reduced in the ratio 35·45 : 35, become 8·997, 24·05, 28·04, 35, 78·94 respectively.

Before the reduction, bromine's value (79·96) was already nearly a whole number, but that is probably quite accidental—for, being a perissad, its atomic weight should be an odd number.

(D). The fourth deduction is that the weight of an atom of Cl, together with its condensed protyle, has been correctly ascertained to be 35·45; but that, when the atomic weight of another element is being compared with and obtained from that of Cl, the latter should be taken as 35 instead of 35·45.

9. The ninth observation is that the constitution and structure of each element can be deduced in a rational and uniform manner by taking into consideration all the above observations and deductions, and the portion of each element which is metallic is thereby made evident.

The constitution and structure of several elements will now be given, as obtained in accordance with the observations and deductions given above.

THE

APPLICATIONS OF GRIGNARD'S REACTION.*

By ALEX. McKENZIE, M.A., D.Sc., Ph.D.

(Concluded from p. 169).

Section II.

Preparation of the Grignard Reagent.

It is of paramount importance that the materials used in the preparation of the Grignard reagent should be as dry as possible. The following description of the preparation of magnesium methyl iodide is given by Grignard (*Revue Générale des Sciences*, 1903, xiv., 1041). The magnesium (24 grms. 1 atom) is placed in a round-bottomed flask to which are attached a dropping-funnel and a reflux condenser. Merthyl iodide (1 mol.) is mixed with an equal volume of anhydrous ether and 25 to 30 cc. of the mixture added to the magnesium. After a few minutes a vigorous action takes place, and at this stage 200 to 250 cc. of anhydrous ether are added; the rest of the mixture of methyl iodide and ether is then gradually added by means of the dropping-funnel. Finally the mixture is warmed if necessary—that is, if the magnesium has not already been all dissolved. Under these conditions one obtains an almost colourless liquid, and there is practically no sediment.

In preparing magnesium methyl iodide in much smaller quantity than indicated by Grignard in the preceding description, the magnesium may be placed in a round-bottomed flask, connected with a condenser, which is provided with a tube, containing calcium chloride and soda lime. The mixture of methyl iodide and about four times its volume of ether is then added in one lot to the magnesium. The action is moderated, if necessary, by immersing the flask in ice-cold water.

The following points regarding the preparation of the reagent may be noted:—

1. *Magnesium.*—Powder, ribbon, or filings are employed by various investigators. The filings, provided by the Aluminium- and Magnesium-Fabrik, Hemelingen, bei Bremen, are very suitable; according to Klages they contain 99·7 to 99·8 per cent of magnesium. Evidence is not wanting to show that impurities in the magnesium sometimes affect the reaction. Beckmann (*Ber.*, 1905, xxxviii., 904) shows that calcium may be substituted in certain cases for magnesium, but the method does not appear to present any advantages over the usual one.

2. *Ether.*—The ether should be thoroughly dried by the following method, for example. Wash with water, dry with calcium chloride, filter, add sodium wire, distil over sodium wire and then over phosphorus pentoxide (compare Perkin and Pickles, *Trans. Chem. Soc.*, 1905, lxxxvii., 647). Ullman and Münzhuber (*Ber.*, 1903, xxxvi., 406) prepare their anhydrous ether by shaking 300 cc. of ordinary ether (sp. gr. 0·722) with a mixture of 25 cc. of concentrated sulphuric acid and 25 cc. of water and then allowing the product to remain for one to two hours over a little sodium wire.

The presence of the merest trace of water is shown up, in the carrying out of a Grignard action, by the slight turbidity which appears when the action starts, and which thereafter disappears.

That the method of drying the ether may have an important influence on the progress of the action is indicated by the experience of Ahrens and Stapler (*Ber.*, 1905, xxxviii., 1296, 3259). In their first communication on the use of dihalogenides those authors showed that ethylene dibromide readily interacts with magnesium and ether to form the compound $MgBr.CH_2.CH_2Br.(C_2H_5)_2O$. Since, however, on repetition of this experiment with the same samples of magnesium and ethylene dibromine the chief product was magnesium bromide, it was obvious that the action

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

depended on the state of the ether. Experiments showed how varying the results were, according to the manner in which the ether was dried.

It should also be remembered that the ether may contain negative catalysers, which may either retard the action or prevent it. Bischoff points out, for example, that magnesium is not dissolved by a mixture of ethylene dibromide and ether in the presence of a little acetone or acetophenone when the mixture is allowed to remain for a night at the ordinary temperature or when it is boiled (*Ber.*, 1905, xxxviii., 2078). This action of a negative catalyser very likely accounts for the fact that occasionally one investigator finds the preparation of some particular Grignard reagent to proceed with ease, whilst another encounters difficulties.

3. *Halogen Compound.*—This ought also to be as free from moisture as possible. It does no harm to distil before use.

The ease with which the Grignard reagent is made depends on the particular halide used. Sometimes the action begins of its own accord with readiness, as in the case of magnesium methyl iodide. Sometimes the mixture requires to be heated, but when once started the action proceeds to a completion after the source of heat has been withdrawn. In other cases the mixture must be continuously heated. Occasionally a catalyser is necessary to start the action vigorously.

It frequently happens that, in addition to the formation of the Grignard reagent, a secondary reaction takes place, namely, the formation of saturated hydrocarbons by the action of magnesium on the halide, for instance, $2C_6H_5Br + Mg = MgBr_2 + C_6H_5.C_6H_5$ (Tissier and Grignard, *Comptes Rendus*, 1901, cxxxii., 835; Tschelinzeff, *J. Russ. Phys. Chem. Soc.*, 1904, xxxvi., 549; Tiffeneau, *Comptes Rendus*, 1904, cxxxix., 481). Diphenyl is always formed in this manner in the preparation of magnesium phenyl bromide. With alkyl halides with low molecular weight this secondary reaction is not pronounced, but with halides of higher molecular weight it is difficult to work with calculated amounts owing to this reaction taking place to a marked extent. According to Grignard (*Ann. Chim. Phys.*, 1901, xxiv., 450; Houben, *Ber.*, 1903, xxxvi., 2897), magnesium, allyl iodide, and ether give the compound $C_3H_5MgI.C_3H_5I$, that is, all the metal is not attacked in the action.

4. *Importance of Completing Solution of the Magnesium.*—It is not desirable to use a Grignard reagent containing an excess of the halide; calculated amounts of magnesium and halide should be used and the solution of the magnesium completed so far as possible. It should be noted that action between magnesium alkyl halide and excess of alkyl halide can take place with formation of hydrocarbon, $RMgBr + RBr = MgBr_2 + R.R$ (Houben, *Ber.*, 1903, xxxvi., 3084).

5. *Substitution of other Solvents for Ether.*—It may be at once stated that ether is by far the most convenient solvent.

Brühl shows that bromocamphor, for example, when mixed with benzene or xylene, dissolves magnesium at elevated temperatures (*Ber.*, 1903, xxxvi., 668, 4272; 1904, xxxvii., 746; Malmgren, *Ber.*, 1903, xxxvi., 2608). Anisole (Malmgren, *Ber.*, 1903, xxxvi., 2619; Houben, *Ber.*, 1905, xxxviii., 3019), amyl ether (Hibbert and Sudborough, *Trans. Chem. Soc.*, 1904, lxxxv., 933), and toluene (Bodroux, *Comptes Rendus*, 1904, cxxxviii., 700) have also been substituted for ethyl ether in certain reactions. Tschelinzeff (*Ber.*, 1904, xxxvii., 2081) shows that, in the formation of Grignard's reagent, ether may be replaced by dimethylaniline. The reaction between dimethylaniline (2 mols.), ethyl iodide (1 mol.), and magnesium (1 atom) is assisted by the addition of a trace of iodine, but the magnesium does not dissolve so quickly as when ether is used. The method was used for the preparation of phenyl ethyl carbinol from benzaldehyde and of phenyl methyl ethyl carbinol from acetophenone. That tertiary amines do actually combine with magnesium organic compounds was subsequently shown by F. and L. Sachs (*Ber.*, 1904, xxxvii., 3088), who obtained, for example, the compound C_9H_7N,C_6H_5MgBr by the action of an ethereal solution of magnesium phenyl bromide on quinoline. Tschelinzeff (*Ber.*, 1904, xxxvii., 4534; *Chem. Zeit.*, 1906, xxx., 378), arguing that tertiary amines form compounds of the type RRRN.RX, has accordingly devised the following modification in the preparation of the Grignard reagent, where a tertiary amine acts as a catalyser. Inert solvents, like benzene, toluene, xylene, hexane, light petroleum, and various terpene hydrocarbons may be used in place of ether if a few drops of a tertiary amine are added. In the case of benzene the following procedure is adopted. The mixture of anhydrous benzene, halogen compound magnesium, and a drop or two of dimethylaniline is heated to boiling until the beginning of the reaction is indicated by the appearance of white flakes; the reaction then proceeds without the application of external heat, and is finally completed by heating. The addition of a little iodine facilitates the starting of the action. In spite of the insolubility of the product, which separates as the type R.MgX, it is claimed that the action is much more energetic and often proceeds more quickly than when ether is used. Further, in those cases where the reagent is formed with difficulty by the ordinary method, the higher temperature at which the Tschelinzeff reagent is formed would appear to be an advantage.

The author of this report has tried the Tschelinzeff method, with little success, however. In spite of what is claimed for it, the method, so far at least, has a theoretical interest only: it does not appear to have been applied at all, except in the very few cases mentioned by Tschelinzeff himself.

6. *Acceleration of the Formation of the Reagent.*—Tissier and Grignard (*Comptes Rendus*, 1901, cxxxii., 1182) found that, whilst alkyl bromides or iodides in ethereal solution as a rule readily interact with magnesium, the action with aryl halides is accelerated by heating or by the addition of a trace of iodine. A drop of methyl iodide serves the same purpose (Klages, *Ber.*, 1904), xxxvii., 1449); this may be used, for example, in the preparation of magnesium α-naphthyl bromide. Iodine and methyl iodide are the catalysers generally used. Monochlorides may not interact with magnesium and ether alone, but do so when a trace of iodine is added (Compare Hesse, *Ber.*, 1906, xxxix., 1146). Aluminium chloride and hydriodic acid may also be used as catalysers (Zelinsky, *Journ. Russ. Phys. Chem. Soc.*, 1903, xxxv., 399). An interpretation for the use of iodine in the formation of magnesium organic compounds from chlorides is advanced by Wohl, namely, $2RCl + MgI_2 = 2RI + MgCl_2$, $2RI + 2Mg = 2RMgI$, $2RMgI + 2RCl = 2MgCl + 2RI$ (*Ber.*, 1906, xxxix., 1952).

In cases where interaction with the halide could not be effected by the usual methods, special devices have been employed. Thus, Ehrlich and Sachs (*Ber.*, 1903, xxxvi., 4296) found that an ethereal solution of *p*-bromodimethylaniline is not acted on by magnesium even when the mixture is heated for several days in the presence of a little iodine. The interaction, however, was brought about as follows:—The magnesium is covered with absolute ether and ethyl bromide added; the action soon becomes vigorous, as usual, and is then moderated by cooling the flask in ice-cold water; the supernatant liquid is poured off quickly from the magnesium and an ethereal solution of *p*-bromodimethylaniline is then added. By this treatment the magnesium had been rendered more active, and the magnesium compound desired was readily obtained by gentle warming. The fact, however, that the yield was far from quantitative, and that the product was necessarily mixed with a little magnesium ethyl bromide, occasioned v. Baeyer to try other methods to make the magnesium active (*Ber.*, 1905, xxxviii., 2759). This result is attained when the magnesium is coated with a thin layer of its iodide. Magnesium filings were heated in a round-bottomed flask over a free flame with constant shaking and half the weight of iodide gradually added. The tem-

perature must not be so high as to cause the mass to melt. With 10 grms. of magnesium this operation requires from fifteen to thirty minutes. The product obtained must be protected carefully from moisture. This "activirtes" magnesium was used by Baeyer himself for the preparation of the magnesium compounds of the iodoanilines and iododimethylanilines, and good results were also obtained by Gomberg and Cone (*Ber.*, 1906, xxxix.. 1467), with diphenylbromomethane when other methods failed.

Kay and Perkin find that commercial magnesium powder sometimes does not interact with *iso*propyl iodide in ethereal solution (*Trans. Chem. Soc.*, 1905, lxxxvii., 1081). When, however, the magnesium is left in contact with an ethereal solution of methyl iodide until the action is vigorous, then washed thoroughly with ether, and at once mixed with the ethereal solution of *iso*propyl iodide, the action proceeds satisfactorily.

7. *Importance of Preventing Oxidation of the Reagent.*—It should be noted that Bouveault and Bodroux have found that the Grignard reagent is acted on by oxygen to form primary alcohols or phenols, so that not only should the reagent be protected from moisture and carbon dioxide, but it should not be left unnecessarily long in contact with air before being applied. Sometimes, indeed, it is necessary to prepare the reagent in an atmosphere of hydrogen (Tschitschibabin, *Ber.*, 1905, xxxviii., 561; Tschelinzeff, *Ber.*, 1906, xxxix., 774).

Methods of Applying the Grignard Reagent.

As a general rule, the compound to be acted on is dissolved in anhydrous ether and the solution either added to the Grignard reagent or *vice versâ*. It is convenient to perform this operation by means of a syphon, and to take precautions that moisture and carbon dioxide are excluded. As a rule, the action requires to be regulated, otherwise it may become too violent. When the addition is complete, sometimes the mixture is heated. Powdered ice is then gradually added, then mineral acid. The product of the action is generally in the ethereal solution.

The following description, taken at random, is typical. It is the method used by Ullmann and Münzhuber for the preparation of triphenylcarbinol from methyl benzoate (*Ber.*, 1903, xxxvi., 406).

A mixture of magnesium (7·2 grms), freshly distilled bromobenzene (57·2 grms., 2·5 mols.), anhydrous ether (60 to 70 grms.), and a trace of iodine is placed in a large round-bottomed flask provided with a reflux condenser and then gently warmed. As soon as the brownish liquid is decolorised and is boiling rapidly it is cooled by immersing the flask in ice-cold water; the action is regulated so that the boiling continues to be vigorous. After twenty minutes the bulk of the magnesium is dissolved; it is practically all gone after the boiling has been continued for half-an-hour longer. The flask containing the reagent is then placed in ice-cold water, and by means of a dropping-funnel a solution of 20 grms. of methyl benzoate (freshly distilled) in an equal volume of anhydrous ether gradually added. The action is vigorous. After the addition of the ester the mixture is heated to boiling for about an hour, ice-cold water gradually added, and then dilute sulphuric acid. The ether is expelled from the ethereal solution, and the product distilled in steam to remove unchanged bromobenzene and a small amount of diphenyl; the triphenylcarbinol remains in the flask. Yield of crude product, 33 grms. (87 per cent); when crystallised from alcohol 28 grms. of pure product are obtained.

Of course this method of working cannot always be adopted. Water in some cases must not be added to the product of the action (compare Kipping's work on silicon compounds). Again, in the action of carbon dioxide and other gases on the Grignard reagent special methods have to be used. Occasionally the temperature at which the reaction is conducted is maintained below 0° (Kohler and Heritage, *Am. Chem. Journ.*, 1905, xxxiii., 21). Sometimes ammonium chloride solution is used in place of mineral acid after the addition of ice (Tilden and Stokes, *Trans. Chem. Soc.*, 1905, lxxxvii., 837); thus in the preparation of phenylmethyltriazene by the action of magnesium methyl iodide the action of acid must be avoided, otherwise the very labile diazoamino-compound undergoes decomposition (Dimroth, *Ber.*, 1903, xxxvi., 909; 1905, xxxviii., 670; compare also Klages, *Ber.*, 1905, xxxviii., 2219).

A perusal of the literature shows that it is often by no means immaterial whether the Grignard reagent is added to the compound to be acted on, or *vice versâ*. This is especially true when one deals with a compound presenting several points of attack for the Grignard reagent. This aspect does not appear to have been fully recognised by a considerable number of investigators in this field. Further, the heating of the product obtained after mixing the Grignard reagent and substance acted on often has an important bearing on the result.

Section III.

Theoretical.

The formation of Grignard's reagent was first represented by an equation such as $CH_3I + Mg = CH_3MgI$ (Grignard, *Comptes Rendus*, 1901, cxxxii., 558), and it is convenient to interpret the various reactions as being due to the type R.MgX. The fact, however, that the reaction takes place with such ease in the presence of absolute ether suggested to Grignard himself ("Thèses sur les Combinaisons Organomagnésiennes Mixtes et leurs Applications à des Synthèses," Lyon, 1901) and to Blaise (*Comptes Rendus*, 1901, cxxxii., 839) that the ether is not simply a solvent in the ordinary sense, but is one of the necessary materials for the action. If the reaction product obtained from magnesium, ethyl iodide, and ether is heated under diminished pressure in a current of hydrogen, the residue contains the compound $C_2H_5MgI,(C_2H_5)_2O$, in which the ether is so firmly bound that it is only partially eliminated when the compound is heated under diminished pressure at 100—125°. The compound $C_2H_5MgBr,(C_2H_5)_2O$ exhibits a similar stability towards heat.

Whereas Grignard and Blaise at the time regarded the ether in these compounds as playing the rôle of ether of crystallisation, Baeyer and Villiger (*Ber.*, 1902, xxxv., 1201) formulate the compounds in question on the basis of the quadrivalency of oxygen, thus: $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}MgR\\X\end{matrix}$. Where R represents the alkyl or aryl group, and X the halogen atom. The existence of oxonium compounds, such as $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}SnCl_3\\Cl\end{matrix}$ and $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}C(C_6H_5)_3\\C(C_6H_5)_3\end{matrix}$ (Gomberg), is adduced in support of this view. Again, Ahrens and Stapler (*Ber.*, 1905, xxxviii., 3259) formulate the compound obtained from ethylene dibromide thus:—

$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}Br\\Mg.CH_2.CH_2Br\end{matrix}$$

The theoretical aspect of the Grignard reaction has been pecially studied by Tschelinzeff. In an early paper he concludes that the ether in the preparation of the Grignard reagent in the usual manner plays the part of a catalyser (*Ber.*, 1904, xxxvii., 4534). He found that interaction between magnesium and alkyl halides took place in benzene solution only when the mixture was heated strongly. In the presence of a little ether (or of anisole), however, the reaction took place at a much lower temperature, at which no action occurred when the ether (or anisole) was absent; the action was very slow, requiring from one to two days for its completion. The white mass which separated contained no ether, exhibited all the ordinary reactions of magnesium organic compounds, and was formed in considerable yield. The point is that this effect was produced by means of a small amount of ether.

Reference has already been made in Section II. to Tschelinzeff's use of tertiary amines as catalytic agents. In a subsequent communication (*Ber.*, 1905, xxxviii., 3664), Tschelinzeff describes thermo-chemical experiments in

which the heat evolved by the action of ether on the ether-free compounds obtained by this catalytic method was measured :—

$$RMgI + \frac{C_2H_5}{C_2H_5}>O = \frac{C_2H_5}{C_2H_5}>O<\frac{MgR}{I} + T.$$

The formula of Baeyer and Villiger is preferred to $\frac{C_2H_5}{C_2H_5}>O<\frac{MgX}{R}$ (Grignard), or to the representation from Werner's standpoint, $\left(\frac{C_2H_5}{C_2H_5}>O \ldots MgR\right)X$ (*Annalen*, 1902, cccxxii., 261 ; the theory of the Grignard reagent is also discussed by Abegg, *Ber.*, 1905, xxxviii., 4112). Although ether is not readily eliminated from the complex $\frac{C_2H_5}{C_2H_5}>O<\frac{MgR}{X}$, it is possible to study the heat effect produced by the change—

$$(C_2H_5)_2O + RMgX = \frac{C_2H_5}{C_2H_5}>O<\frac{MgR}{X},$$

since it is possible to prepare the "individual" magnesium compounds free from ether. Tschelinzeff concludes that in the preparation of the Grignard reagent by the ordinary method there are two distinct reactions :—(1) The formation of the magnesium alkyl (or aryl) halide, and (2) the transformation of this into an ether complex.

Tschelinzeff (*Ber.*, 1906, xxxix. 773) next points out that, after all, those ether complexes were characterised by Grignard and Blaise subsequently to heating the Grignard reagent under diminished pressure. It is not justifiable to assume, as is generally done, that those same complexes actually exist under the conditions which obtain when the Grignard reagent is made in the usual manner. Tschelinzeff, in his previous paper (*loc. cit.*), although actually showing that at least one ether complex is formed, does not prove that the formation of additional complexes is impossible. Now Zelinsky (*Journ. Russ. Phys. Chem. Soc.*, 1903, xxxv., 399) has obtained the compound $MgI_2,2(C_2H_5)_2O$, and Tschelinzeff the compound $MgI_2,4(C_2H_5)_2O$. The analogy is accordingly drawn between the formulæ $(C_2H_5)_2O1.Mg.I(C_2H_5)_2O$ and $R.Mg.I(C_2H_5)_2O$.

Now, since the magnesium iodide complex, $[(C_2H_5)_2O]_2I.Mg.I[(C_2H_5)_2O]_2$, is known, the question naturally suggested itself as to the possibility of analogous ether complexes of the type $R.Mg.I[(C_2H_5)_2O]_2$. The compounds $C_3H_7MgI,2(C_2H_5)_2O$ and $C_5H_{11}MgI,2(C_2H_5)_2O$ were accordingly isolated.

These results, based on analytical and thermo-chemical experiments, prove conclusively, according to Tschelinzeff, that in the preparation of magnesium organic compounds by Grignard's method one obtains ether complexes with two molecules of ether, for which the formulation $\frac{C_2H_5}{C_2H_5}>O<\frac{MgR}{I:O}<\frac{C_2H_5}{C_2H_5}$ is suggested (compare also Tschelinzeff, *Ber.*, 1906, xxxix., 1674, 1682, 1686).

Tschelinzeff (*Ber.*, 1907, xl., 1487) also shows that the "individual" magnesium organic compounds are also capable of forming complexes with tertiary amines, thus : $RRRN<\frac{MgR}{I}$. These aminates are analogous to monoetherates. No complexes have yet been described analogous to dietherates.

The question of the constitution of the oxonium compounds formed in the preparation of the Grignard reagent by the ordinary method is still, however, under discussion. Tschelinzeff (*Comptes Rendus*, 1907, cxliv., 90) points out that if Baeyer's formulation, $\frac{R}{R}>O<\frac{MgR'}{X}$, is accepted, two isomerides are possible, namely, $\frac{R}{R}>O<\frac{MgR'}{X}$ and $\frac{R}{R'}>O<\frac{MgR}{X}$; whereas if Grignard's formulation, $\frac{R}{R}>O<\frac{MgX}{R'}$, is correct no isomerism is possible. Tschelinzeff claims to have established the existence of isomerides. Grignard, however (*Bull. Soc. Chim.*, 1907, [4], i., 255), maintains that his formula permits of the conception of isomerides, and regards it as more plausible than Baeyer's.

THE QUANTITATIVE SYNTHESIS OF ARGENTIC NITRATE, AND THE ATOMIC WEIGHTS OF NITROGEN AND SILVER.*

By THEODORE WILLIAM RICHARDS
and
GEORGE SHANNON FORBES.

Introduction.

The composition of argentic nitrate is one of the questionable premises in the lively argument which has recently taken place concerning the atomic weights of nitrogen and silver. (See especially Guye, "Nouvelle Rech. s. l. Poids Atom. de l'azote," Soc. Ch., Paris, 1905. The reader is referred for a convenient *résumé* to the "Report of the International Committee on Atomic Weights," *Journ. Am. Chem. Soc.*, 1906, xxviii., 1, and many other places; also to Clarke, *Journ. Am. Chem. Soc.*, 1906, xxviii., 293 ; Gray, *Trans. Chem. Soc.*, 1906, lxxxix., 1173). Although Stas's syntheses of this salt were carried out on a large scale, and far more carefully than those of anyone before him, several points concerning the details of the work were not investigated with the care which modern physico-chemical knowledge demands. Accordingly, a repetition of this work of Stas's seemed to be worth the trouble involved, and the following pages contain a brief account of nine months' thought and labour upon it.

The method appears at first sight to be extremely simple, consisting merely in the weighing of pure silver, the dissolving of this silver in nitric acid, and the weighing of the resulting nitrate. The preparation of pure silver having been already solved, the great difficulty consisted in the procuring of satisfactory evidence that the nitrate was free from impurity, and in making sure that none of the silver was lost during the process. The main emphasis of the subsequent discussion will therefore be laid on these points, the other details being often indicated with but few words, because they so closely resemble the details of previous investigations carried out in the Chemical Laboratory of Harvard College.

The research naturally divided itself into four sections, namely, first, the preparation of pure materials; second, the quantitative synthesis ; third, the determination of the purity of the product ; and fourth, the final result and its relations to the table of atomic weights. These will be considered in order.

Preparation of Pure Materials.

All the substances used in the research were purified with very great care. Nitric acid and silver were the two most important.

Nitric acid was supplied by two firms. Each sample was warranted by the manufacturers to be of a very high grade of purity. Each was re-distilled twice just before adding to the silver, using only the middle portion of each distillate. None of the samples left a trace of non-volatile residue on evaporation. No difference could be detected in the results because of the difference of source of the acid, nor was the constancy destroyed when a single distillation only was made (Experiment 11). Hence little anxiety was felt concerning the purity of this material.

Silver.—The researches of Richards and Wells have shown how to prepare silver of unquestioned purity. Preliminary determinations 1, 2, 3, 4, 5, 7, and 8 were made on a sample (A) left over from the above-mentioned research, crystallised fifteen times with nitric acid, precipitated with formate, and fused on purest charcoal, but

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not electrolysed or fused in hydrogen. No. 9 was made with a sample prepared by Prof. Baxter for his final work on bromine. It had been through the chloride and formate treatment, electrolysed, fused in hydrogen, cut with a saw, etched with nitric acid, boiled with water, dried at dull redness *in vacuo*, and given us ready to weigh. We are much indebted to him for furnishing this check on our silver. The final determinations were made with silver derived from several preparations. The first of these (C) was re-crystallised sixteen times as nitrate from water and re-distilled nitric acid, and then precipitated twice in succession with formate. A part of the final formate product was fused on the best lime in carefully purified hydrogen made from aluminium and sodic hydroxide. Sample D had been precipitated as chloride, reduced with best alkaline sugar, washed free from chloride, dissolved in nitric acid, filtered, and crystallised as nitrate in platinum six times from nitric acid distilled in a platinum condenser. Centrifugal treatment eliminated the mother-liquor. The last crop of crystals was precipitated with formate in a silver dish, washed free from ammonia, and fused in a cup of pure lime. Sample F was obtained by the electrolysis of a button of very pure silver from Colorado, which had been fifteen times re-crystallised as nitrate, precipitated with formate, and fused on lime. Samples C, D, and F were all cleaned by etching, and then purified by electrolysis through a nitrate solution made from some of the same silver and the purest nitric acid. They were then fused separately, on a well-seasoned lime boat, in a new porcelain tube, in an atmosphere of pure electrolytic hydrogen. The Hempel stoppers fitted so well that the pressure could easily be reduced to a fraction of a millimetre by a Geryk oil-pump when desired. The heating was accomplished by a large Heraeus electric furnace which fused the silver without overheating any part of the tube. In all cases the initial fusion was completed in hydrogen at atmospheric pressure, but in half the fusions the tube was evacuated before the temperature was lowered. No spirting or boiling could be observed through the glass window when the pressure was reduced, and the silver thus prepared gave the same combining weight as that cooled under a full atmosphere's pressure of hydrogen. Thus the conclusion of Richards and Wells, and of Baxter, that silver cannot dissolve a weighable amount of hydrogen, was confirmed.

The buttons thus obtained were etched to remove lime, and if too large to go into the flasks used for the synthesis, were cut with a cold chisel or a jeweller's saw, observing all the precautions recommended by Richards and Wells. The fragments freed from superficial iron were washed and dried, sometimes in the electric oven in air at 150° for an hour, sometimes in a vacuum at dull redness, and sometimes in a reduced pressure of hydrogen. Judging from the constant combining weight, all these methods were equally good.

Water.—The water was distilled first with alkaline permanganate through a glass condenser, and then, after the addition of a small drop of dilute sulphuric acid, through a carefully cleaned condenser of block tin. Needless to say, dust was excluded as much as possible, and distillations were conducted immediately before the water was needed, in order to avoid absorption of gases or solution of solid matter.

Air.—It will be remembered that Stas allowed his solutions of argentic nitrate to evaporate very slowly, the vapours diffusing out through the neck of his flask, and condensing in a suitable receptacle. Under these conditions the evaporation required seventy-two hours of continuous heating—an unnecessarily prolix process. To hasten the escape of aqueous vapour, it was resolved to maintain a gentle current of pure dry air throughout the process. The air for this purpose was delivered from a water-pump, which must have removed some of the original impurities. It was passed first through a tall Emmerling tower filled with beads moistened with concentrated sulphuric acid, to which a trace of potassic bichromate had been added, and then through two more towers filled with a concentrated solution of pure potash, being thus freed from ammonia and from acid gases. Next it was passed through a tall drying tower of stick potash, to a hard glass tube containing platinised asbestos heated to dull redness by a Bunsen burner. The hot platinum was intended to destroy organic matter. Hence it passed into a trap designed to catch asbestos shreds, and finally, the air was dried by two towers of broken potash. The whole purifying train was put together without rubber, all the pieces being blown together except the hard glass tube, which was connected with the soft glass on either side with joints so well ground that no lubricant was necessary. The towers were glass-stoppered. Air thus purified and dried contains nothing to injure the silver nitrate except possibly a minute trace of ammonia, which might have come out of the potash solutions.

The Synthesis of Argentic Nitrate.

The materials having been prepared, the next step was to combine them. This combination must take place in a vessel wholly free from a suspicion of solubility on the one hand, and arranged so as to prevent loss of material on the other hand. At the same time, it was important to be able to evaporate and to weigh the argentic nitrate in the same vessel. After a careful consideration of the somewhat conflicting claims of these requirements, it was decided to carry out the process in small round-bottomed flasks of fused quartz of from 0·03 to 0·04 litre capacity; with necks 11 cm. in length and 6 to 9 mm. in internal diameter. Collars of platinum-wire provided with loops permitted the suspension of these flasks from the hook of the Troemner balance. Before weighing, they were heated in the oven, to be presently described, to 250° for at least half an hour, a moderate air-current sweeping through them all the time. The coverings were then lifted, and each flask was removed by a hook of platinum-wire sealed into a glass rod, and transferred to a large desiccator provided with a suitable support. Two flasks similar in weight and surface were treated in the same way, and kept in the same desiccator. After two hours near the balance the first flask was weighed against a tare, its weight being determined by substitution of the first by the second flask and a few small weights. Upon removal from the desiccator both flasks absorbed moisture from the air, often to the extent of 0·0001 grm., but they soon reached constancy with respect to one another, which was all that was needed. No final weighings were made when the hygrometer in the weighing-room stood above 40, and under these circumstances flasks could be weighed on successive days with variations not exceeding 0·00003 grm.

A new Troemner balance, sensitive to 0·01 mgrm., was available for the research. The brass weights were carefully standardised at the beginning at the year, and again upon starting the final series; and the rider also was calibrated, and the necessary correction employed. For correction to the vacuum standard 0·000132 was added to each apparent grm. of argentic nitrate, and 0·000030 was subtracted from each apparent grm. of silver. This was on the assumption that the two specific gravities concerned were respectively 4·35 and 10·49, that of the brass weights being 8·3.

The silver was now weighed by substitution, and carefully pushed down the neck of the flask, which was held meanwhile in a horizontal position to avoid breakage. Next the whole was transferred to a large clean empty desiccator, whose sides had been moistened, and the flask was laid on a suitable support of glass and platinum tilted 45° from the vertical. A sufficient quantity of purest nitric acid mixed with half its volume of distilled water was poured in from the platinum crucible into which it had just been distilled. The cover of the desiccator was replaced, but its stopper was first removed, and covered with a watchglass and a clean beaker. The apparatus was now kept all night in a warm place, between 40° and 50° C.; thus the silver when dissolved remained in solution, though the volume was restricted to 2 cm. of solution per grm. of

nitrate. In the morning the process was found to be complete. After washing down the neck with a few drops of freshly distilled water, the flask was placed in the oven as before. The desiccator was washed with a little water, the washings being tested for silver in the nephelometer; if any had been found it might have been feared that more had escaped, but as no trace was ever found, it was inferred that the long inclined neck had caught all the spray.

Attention is now called to the apparatus for evaporation. (In passing it might be noted that one of us used a somewhat similar arrangement for evaporating solutions of sodic sulphate fifteen years ago, *Proc. Amer. Acad.*, 1891, xxvi., 258). The main feature of this was the combined delivery tube for the air current and hood for the protection of the contents of the flask. This hood, H, with its ingress and egress tubes, I and E, is shown in the diagram (Fig. 1).

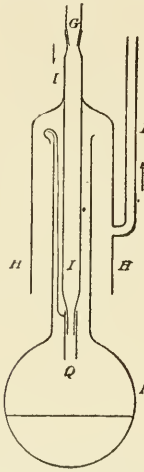

FIG. 1.—APPARATUS FOR EVAPORATING AQUEOUS SOLUTIONS. (Section about half actual size).

F, flask of fused quartz; H, H, protecting hood, with tube, I, for air supply; Q, quartz tube suspended by platinum wire, serving as air nozzle.

The dry air used to sweep out the aqueous and nitrous vapours entered from the purifying train at G, where connection was made by a well-ground joint; passing through the tube I, it escaped into the body of the flask and out through its neck. A side tube, E, was attached to H for connection with a water-pump. The flask rested on a triangle of platinum-wire attached to a glass tripod, and the whole was placed in a 1·5-litre beaker which served as the oven. A sand-bath enabled this to be kept at any desired temperature. The cover of the beaker was of sheet copper, pierced with three holes, for the tubes I and E, and for the thermometer. As no nitrous fumes escaped into the oven, this cover remained intact. In the preliminary trials the extra tube Q was lacking, the tube I being extended to take its place. The part which had projected into the body of the flask was treated with hot dilute nitric acid, and investigated for silver in the nephelometer. Occasionally some was found, but the corrections required were not large. Nevertheless, the possibility that the fused nitrate had attacked the glass was always disturbing, and the inconvenience and uncertainty of this correction made its elimination desirable. Accordingly, in the final determinations, a section of quartz tubing, Q, 3 mm. in diameter and 15 mm. long, was firmly attached to a platinum-wire and lowered till it barely projected into the body of the flask. This supporting wire hooked into the collar, so that the quartz tube could be removed while the silver was dissolving. During the evaporation, however, it was in place, and the end of the glass delivery tube was shortened and drawn down to fit into it. The glass tube was still tested as before, but no silver was ever recovered from it. Hence the flask and the quartz tube must have retained all the silver originally weighed out.

The evaporation of the liquid was easily and quickly conducted in this apparatus. If the flask was not more than half full, and the air passed through the drying train no faster than two bubbles per second, it was possible to maintain the temperature of the oven at 125° without risk of ebullition. The vapours drawn out as before described passed first through a U-tube filled with moist glass beads and just sealed with water, afterwards through a tower of caustic alkali to take out nitric acid which might attack the water-pump. When the liquid became coated with a film of crystals the temperature was lowered to 110°; bubbles of vapour now formed gradually under the crystal layer, and the slight spattering caused by their rupture could be seen on the inside walls of the flask. The oven was now suddenly cooled, so that the vapours from the hot liquid, condensing on the walls of the flask, washed down the crust which had formed during evaporation. Upon continuing the heating, a porous crust was soon formed, under which the formation of steam caused no spattering. Finally, the temperature was raised gradually, while the last trace of liquid was disappearing. The solid was dried for a quarter of an hour at 150° in the dark, and then heated to 230° to insure complete fusion, not only of the main portion, but also of any portions projected on the upper walls of the flask. (This temperature, 230°, and the others to be recorded later have not been corrected for the exposed steam; they do not indicate the exact melting-point of the salt). The temperature was soon lowered to 210°, which sufficed to keep the mass in fusion, and the air current was continued for an hour. Then, in subdued light, the flask was lifted out by a loop of platinum-wire passed through its collar, placed on a network of platinum-wire, and tilted in all directions to cause the nitrate to solidify in a thin layer on the walls. Once this precaution was neglected, and the flask was cracked by the contraction of the nitrate on cooling. When the nitrate was wholly solid but still hot, the flask with its contents was transferred to its support of platinum wire in a large tight desiccator, which was wrapped in a black cloth and left near the balance over-night. Then the weight of the flask was determined as before. Thus in the entire cycle of operations nothing but platinum, clean glass, and pure air touched the outside of the flask.

It remains to be proved that no silver was carried out by the air current. This was inferred because no trace of silver was ever found in the U-tube through which all the vapours passed; but more definite evidence was obtained by re-dissolving two finished determinations, and evaporating them again with the customary precautions.

Determination No.	$AgNO_3$ once evaporated.	$AgNO_3$ twice evaporated.	$AgNO_3$ thrice evaporated.	Total gain.
8.	10·68933	10·68928	10·68920	−0·00013
15.	14·20114	14·20122	14·20127	+0·00013
			Average gain or loss	0·00000

The first residue in the case of No. 15 was slightly darkened by prolonged heating; still no fixed tendency toward either loss or gain is shown by these figures, and the reliability of the method is demonstrated.

Two preliminary experiments were not finished, and one was rejected because of known error. Six preliminary determinations carried out in the way just described gave results varying from 157·483 to 157·475 parts of nitrate

from 100·000 parts of silver, in the mean 157·479. This is very nearly the same as the final series, given later, but because of sundry irregularities these determinations are individually much less trustworthy than the latter. One of the preliminary determinations was made with a piece of silver kindly given us by Prof. Baxter for the sake of comparison, and for which we are much indebted. It gave a result perhaps higher than the average, but not by an amount greater than the limit of error of the experimentation at that time. It is greatly to be regretted that this piece was not examined after every detail of the process had been perfected, because the comparison would have been interesting, although not at all essential for the completeness of our work.

When it appeared impossible to improve upon the details of the experimentation, a final series of six consecutive determinations was carried out with all possible care. In each case, except Nos. 14 and 15, the argentic nitrate was maintained for an hour in a fused condition while dry air swept over it. In No. 14 only one-quarter of an hour was allowed, whereas in No. 15 the fusion was prolonged for three hours. Sample D of silver was used in Syntheses 10, 11, and 12, and Sample F in the other three.

The Synthesis of Argentic Nitrate.

No. of synthesis.	Weight of fused silver (in vacuum). Grms.	Weight of fused argentic nitrate (in vacuum). Grms.	Weight of argentic nitrate made from 100·000 parts of silver.
10.	6·14837	9·68249	157·481
11.	4·60825	7·25706	157·480
12.	4·97925	7·84131	157·480
13.	9·07101	14·28503	157·480
14.	9·13702	14·38903	157·481
15.	9·01782	14·20123	157·480
	Average		157·480 (*a*)

(*a*) The probable error of this average, computed from the results when carried to the next decimal place, is only 0·0001, a wholly negligible quantity. Hence repetition of the process was unnecessary.

For this ratio just found to be 100·000 : 157·480, Stas obtained an average of 100·000 : 157·475 from nine determinations, which ranged from 157·463 to 157·488.

Better agreement then that exhibited by the above table could hardly be desired or expected, as the greatest deviation corresponded to less than 0·1 mgrm. in the weight of the argentic nitrate. This series demonstrated that it is not necessary to use very large amounts of material in order to attain a very high order of precision, if only the details of experimentation are fittingly arranged.

Satisfactory as this series of results appears to be, it is by no means to be accepted without further question as representing the true weight of argentic nitrate to be obtained from pure silver. Even in this fused salt, prepared under such favourable conditions, several impurities might exist; and because in each case the method of treatment was the same, these impurities might be constant in amount, and therefore not perceivable in the results. Accordingly, attention was now directed to the search for these impurities, and this part of the investigation was found to be the most arduous and time-consuming part of it. The following section discusses this matter.

(To be continued).

Disecondary Butylene Monochlorhydrine.—Louis Henry. — Disecondary butylene monochlorhydrine, $H_3C{-}CH{-}CH{-}CH_3$ (Cl, OH), results from the action of hypochlorous acid, (HO)Cl, upon symmetric dimethyl ethylene, $H_3C{-}CH{=}CH{-}CH_3$. It is a colourless liquid slightly soluble in water; it boils at 138—139° under 753 mm. pressure, and its vapour-density is found to be 3·73 (calculated value, 3·75). It is readily transformed by alkalis and by salts with an alkaline reaction, such as K_2CO_3, into its oxide, $H_3C{-}CH{-}CH{-}CH_3$ (O).—*C. R.*, cxlv., No. 11.

ON THE DIRECT QUANTITATIVE SEPARATION OF CHLORIDES AND BROMIDES.

By LAUNCELOT W. ANDREWS.

Introduction.

The direct separation of chlorine from bromine has always been considered one of the most difficult problems of quantitative analysis, excepting those relating to the rare earths and the radio-active elements. The standard works on quantitative analysis usually content themselves with a discussion of indirect methods, omitting any description of processes for direct separation.

Practically all the methods recommended for the direct separation of these elements rest on oxidation reactions applied to solutions of bromides and chlorides. The difference between the oxidation-potential of a solution of chlorine in potassium chloride and water and that of a corresponding solution of bromine is about 0·241 volt (Bancroft, *Zeit. Phys. Chem.*, 1892, x., 405). Numerous oxidising agents have been employed, always in acid solution, that is in the presence of solutions more or less concentrated as regards hydrogen ions. In every case investigated excepting one the oxidant used possesses a higher oxidising potential than that of an aqueous solution of chlorine. Hence in such cases, the success of the operation must depend on interrupting the process exactly at the point when all bromine is liberated, since if prolonged beyond that point some chlorine would also be set free. Methods subject to conditions of this sort cannot be looked upon as other than empirical. They can give results approximating the truth, only by a minute regard to all the circumstances of the reaction, as temperature, degree of acidity, concentration, &c., and only then by a happy compensation of errors.

Bugarszky (*Zeit. Anorg. Chem.*, 1895, x., 387) first pointed out the necessity of selecting as an oxidant, one of which the oxidising potential should be intermediate between that of chlorine and that of bromine. With this principle in view, he made use of iodic acid as an oxidising agent. It has an oxidation potential 0·064 volt higher, according to Bancroft, than that of an equivalent and equally acidified bromine solution. A very careful examination of Bugarszky's method, in comparison with a considerable number of other methods, has confirmed that investigator's observations in most essential respects, and has convinced me that his is by far the best method yet published. It is true that the process of Engel (*Comptes Rendus*, 1894, cxviii., 1263) is capable of giving reasonably exact results, especially with certain modifications, of which the most important is the exclusion of ammonium salts. The feature of the latter method is the use of a perdisulphate as oxidant. Engel employed the ammonium salt, $(NH_4)_2S_2O_8$. The method has serious drawbacks. One of these is the oxidation of part of the bromide and chloride to bromate and chlorate, which takes place under conditions not easily defined but seemingly due to small amounts of catalysing agents. Since the chlorate and bromate must be afterward reduced and the whole process repeated in order to complete the desired separation, I felt compelled to abandon the method after a good deal of experience with it.

Briefly stated, Bugarszky's method consists in adding to the bromide-chloride solution, sulphuric acid and potassium di-iodate, then distilling. The bromine and iodine liberated in accordance with the equation $KH(IO_3)_2 + 10KBr + 11H_2SO_4 = 11K_2SO_4 + 10Br + 2I + 6H_2O$ passed off with the steam. The remaining solution contains the hydrochloric acid and the excess of iodic acid. Bugarszky observed that when the bromine was determined by absorption of the vapour in potassium iodide and subsequent titration of the iodine, the amount of bromine found was considerably less than that taken, in consequence of a portion having been reduced by the steam to hydrobromic acid with liberation of oxygen. He therefore re-

commends determining the bromine by titration of the unconsumed excess of iodate remaining in the mother-liquor. He overlooks, strangely enough, the fact that if the first named procedure gives too low figures for the bromine, the second must lead to results that are too high, because a part of the bromine being reduced to hydrobromic acid in the solution and in the condensed and returned steam, it must be again oxidised at the cost of the iodic acid. This obvious reasoning is fully confirmed by my experiments, which showed always results too high by titration of the iodate excess (by 1·0 to 1·5 per cent). Hence the determination of the bromine should be made by the alternative method of Bugarszky, viz., absorption of the vapour, containing steam, bromine, and hydrobromic acid, in a reducing solution, with following titration of the bromide according to Mohr or Volhard, or gravimetric estimation.

As regards the determination of the chloride in the mother-liquors, I was able to get results of the same accuracy as the test analyses of Bugarszky. These results are satisfactory when the relative amount of chlorine is large, but were not sufficiently so for my purpose when the chlorine percentage is low. The causes of inaccuracy in this case do not lie in any imperfection of the main reaction, but are as follows:—

1. The maximum amount of substance taken by Bugarszky is 0·400 grm. This cannot well be exceeded without other modifications of the method.

2. The presence of considerable quantities of sulphuric acid and sulphates interferes noticeably with the precision of the Volhard method when the amount of chloride is very small, because appreciable amounts of difficultly soluble silver sulphate are dragged down with the chloride and sulphocyanate.

3. Bugarszky gets rid of the iodic acid before determining the chlorine by first reducing to iodide with sulphurous acid, then expelling the iodine by boiling with sodium nitrite. This procedure is open to objection. It is no easy matter to prepare or to buy sodium nitrite free from chloride. (It is to be remembered that silver chloride is to a considerable extent soluble in solutions of sodium nitrite, hence the salt must be wholly decomposed before testing for chloride). If any trace of nitrous acid is left in the solution it will, as is well known, interfere with the sharpness of the end reaction in the Volhard titration. Further, the process leaves a considerable additional amount of foreign salts in solution, and especially of sulphate, disadvantageous for seasons stated under 2. As a matter of fact, it is not necessary to remove the excess of iodic acid at all. If the solution is sufficiently diluted and acidified with nitric acid, iodic acid only interferes in a minor degree with the titration, the error being of about the same order as that introduced by the presence of sulphates; negligible therefore except when the amount of chloride is small.

To increase the accuracy of the method it accordingly seemed advisable, to increase the amount of substance taken, to replace the sulphuric acid by nitric acid, to remove the excess of iodic acid by a single reagent which would introduce no sulphate or other injurious compound, and the excess of which would require no removal. It would take too much space to recount the steps by which these objects were attained, and several additional advantages incidentally gained. Before presenting details of the procedure finally adopted it will suffice to say that the removal of the iodic acid is best effected by the use of phosphorous acid. This substance possesses almost ideal properties for the purpose. Under the conditions, it reduces iodic acid to free iodine, quantitatively, not leaving even the slightest traces of iodide in the solution. The iodine can be readily boiled off, and the excess of phosphorous acid does not in the least interfere with any subsequent operations. Experience has demonstrated that in expelling the bromine it is not sufficient to distil till the solution is colourless as prescribed by Bugarszky, since at this point traces of bromine may still remain as shown by fluorescein paper (Baubigny), or by the still more sensitive tests mentioned below. It proved to be desirable to use an amount of bromide for the analysis, increasing as the amount of chloride diminishes, and an amount of iodate such that the excess of iodic acid shall be approximately constant. A similar consideration is valid for the nitric acid. The effect of this adjustment is, that when the amount of bromine to be expelled is larger the solution is more acid at the beginning, but the final acidity at the close of the reaction is approximately the same. Hence, it does not take much longer to expel the larger amounts of bromine than the smaller, the reaction being slow only when nearly complete.

For the determination of chloride in crude potassium bromide, the following table will serve as a guide to the amounts of substance and reagent to take. In case of other bromides quantities equivalent to those given should be used.

If the KBr—KCl has per cent of KCl.	Weight of KBr+KCl.	Fifth normal iodate, KIO_3.	Nitric acid, approximately double normal.
	Grms.	Cc.	Cc.
5—10	0·6	36	20
1·5—5	1·8	96	26
0·25—1·5	3·6	186	35

The Analysis.

Select a Kjeldahl flask of 400 to 500 cc. capacity and having a neck 20 to 25 cm. long. Introduce into it the chloride-bromide mixture, add the potassium iodate solution and the nitric acid, and enough water to bring the volume to 200 or 250 cc. Support the flask at an angle of about 30° from the vertical, resting on a hole about 2½ inches in diameter, in a square of heavy asbestos board. The latter is of course intended to deflect the hot flame gases from the sides of the flask. The neck acts as a reflux condenser, returning to the flask traces of hydrochloric acid which might otherwise escape when the volume of the liquid is reduced to its minimum. Heat to gentle boiling with a Bunsen flame. It is advantageous, but not by any means necessary, to begin this operation near the close of a day's work, and after boiling for five minutes to allow the solution to stand over-night. The reaction goes on while standing, and thus shortens the actual period of boiling. In any case, boil down to a volume of about 90 cc. This point should be permanently marked on the outside of the flask in such a way as to correspond to its slope. When the amount of chloride is small, the volume may be reduced to 60 cc. without measurable loss, but in general the 90 cc. mark should not be passed. The boiling ought to go on at such a rate that thirty to forty minutes are required. The solution is now usually perfectly colourless, and only traces of bromine remain. Add 100 cc. of water, and continue the boiling until 50 cc. have passed off. The escaping vapour may now be tested with fluorescein paper, held across the mouth of the flask for five minutes. If no change of colour from yellow to orange occurs, the final test may be made. For this purpose, pass the escaping steam, with the help of a clean rubber stopper and narrow bent glass tube, through 10 cc. of a 2 per cent solution of potassium iodide to which enough decinormal hydrochloric acid has just been added to impart a faint acid reaction, in a test-tube, until the solution has become hot (about forty seconds). If this liquid shows no yellow colour when held against a white surface the bromine may be regarded as expelled. (It is hardly necessary to say that the iodide must be pure and able to stand heating under the conditions prescribed, without any colouration, when bromine is absent). This test is more delicate than fluorescein or than sodium bicarbonate solution faintly tinted with indigo.

When the bromine is all expelled, add, without interrupting the boiling, 1·0 to 1·50 cc. of a 25 per cent solution of phosphorous acid. Continue the boiling till all iodine is

driven off, as shown by the colour, and five minutes longer. This requires about ten minutes in all. At no time may the volume be allowed to become less than 90 cc. (except in the case previously mentioned, when the total amount of chlorine is small, a few mgrms.).

To the water-white and cooled solution in the flask add a moderate excess of twentieth or of fiftieth normal silver nitrate solution (according to the amount of chloride present), then a fragment of the best filter-paper, and shake violently till the paper is reduced to pulp. Filter, wash, add 5 cc. of 10 per cent ferric nitrate solution, and titrate after Volhard with twentieth or fiftieth normal sulphocyanate till coloured, and then back with the silver solution. The end-point can always be more exactly hit in this direction.

The freedom from chlorine of all reagents should be controlled. The standard potassium or ammonium sulphocyanate will not give a sharp end reaction if it contains chloride. It may be tested in the same way as a bromide, *i.e.*, decomposing by boiling with nitric and iodic acids, &c.

The fifth normal potassium iodate solution contains 7·138 grms. of the purest re-crystallised salt to the litre. If preferred, a normal solution may, of course, be employed instead.

The freedom of this salt and of the other reagents from chlorine may best be determined by a blank analysis on 2 grms. of the potassium iodide, using the regular amounts of iodate, nitric acid, and phosphorous acid. Phosphorous acid is the only reagent which cannot be easily found free of chlorine, and the amount used is so small that a trace of chlorine in it does not, as a rule, matter much, as the error so introduced is usually less than 0·01 per cent.

The following analyses of mixtures of known composition will serve to show the degree of accuracy to be expected from the method. A nearly pure potassium bromide, containing 0·025 per cent of chloride, was mixed with varying amounts of potassium chloride, and the mixture then analysed by the method described. The first column gives the weight in grms. of the bromide taken; the second, the weight of potassium chloride added (in the form of a standard solution); the third, the total amount of chloride present; the fourth, the number of cc. of standard silver solution consumed; the fifth, the weight of potassium chloride found; the sixth, the percentage of chloride actually present; the seventh, the percentage of chloride found.

Bromide taken.	Chloride added.	Total chloride.	Silver solution. N/50.	Chloride found.	KCl present.	KCl found.
Grms.			Cc.		Per cent	Per cent.
3·6000		0·0009	0·60			0·025
3·6000	0·0361	0·0370	24·55	0·0366	1·077	1·06
3·6000	0·0722	0·0731	48·82	0·0728	1·991	1·982
			N/20.			
3·6000	0·1083	0·1092	29·32	0·1094	2·945	2·950
3·6000	0·1444	0·1453	39·13	0·1459	3·880	3·896
1·8000	0·1444	0·1449	38·93	0·1452	7·453	7·467

Further, a mixture was made by me of pure potassium chloride and of a potassium bromide containing 0·07 per cent of chloride, both pulverised, dried at 150°, and then thoroughly incorporated in such proportion that the product contained 3·95 per cent of chloride. Portions were then given to three chemists for analysis with no further information beyond the fact that the amount of chloride was between 1·5 and 5·0 per cent. Only one of these chemists had used the method before. They reported the following results:—

Chemist "C" reported 3·93 per cent of chlorine; "S" reported 3·98, and in a duplicate 3·88, with the remark that he thought this "too low, since the evaporation has been carried much too far"; "A," 4·02; "L," 3·96 per cent. There is no doubt that with practice even closer results than this set of analyses indicates can be regularly obtained.

Evidence of this is given by the analyses of crude bromine reported below.

The method has now been in constant use in the laboratory of the Mallinckrodt Chemical Works for six or eight months with uniformly satisfactory results.

Determination of Chlorine in Crude Bromine.

Crude bromine (of American origin) contains chlorine varying in amount from 1 to 13 per cent or even more, a very minute amount of iodine, a small quantity of water (not far from 0·05 per cent), brominated organic matters derived from tallow, and small amounts of tar formed by the action of bromine on coal-tar. Some samples contain an easily recognisable quantity of bromoform, which is left as a nearly colourless liquid when 25 or 50 cc. of the bromine are allowed to evaporate in a current of air.

The percentage of chlorine may be determined by converting the sample quantitatively into a mixture of chloride and bromide by dissolving in caustic soda, evaporating to dryness, fusing in the presence of a little sugar-charcoal, then analysing the melt by the process already given for bromides.

A much shorter, more convenient, and at the same time somewhat more accurate method, consists in treating the weighed sample of crude bromine with a solution of an alkali iodide insufficient to react with all the bromine, but more than sufficient to retain all the chlorine in the sample. No chlorine escapes from this mixture on boiling. The amount of salt to be handled is less than would be the case if all the bromine were converted into bromide, and, consequently a larger sample can be taken, which contributes materially to the accuracy when the percentage of chlorine is very low—for example, a few tenths or even thousandths per cent.

Before describing working details of this procedure, it is appropriate to draw attention to certain precautions necessary to observe in securing samples of the crude bromine for analysis and in handling them when obtained. Special precautions are imposed on account of the ease and rapidity with which the composition changes by evaporation of the chlorine. I have satisfied myself by actual analyses that it is impossible to pour bromine from one bottle to another without a very appreciable diminution in chlorine percentage occurring. The ordinary temperature and an ordinary bromine of from 4 to 6 per cent of chlorine are here understood. A bottle containing about 600 grms., closed with a badly-ground glass stopper, stood in the laboratory about a month, during which period it was opened two or three times just long enough to withdraw a sample for analysis. The chlorine gradually fell from 6·44 per cent to 5·58. Another sample was allowed to stand in a narrow tall cylinder till, by evaporation, its volume was reduced from 50 to 30 cc. This resulted in a diminution of chlorine from 6·2 to 3·4 per cent.

These facts are recorded in order to emphasise the propriety of drawing samples by means of a suitable special pipette, without suction, from beneath the bromine layer, and of avoiding under all circumstances pouring bromine to be analysed from one receptacle to another. When the amount of chlorine exceeds 2 per cent, it is well to cool the bromine bottle in ice-water before taking the sample.

A suitable form of pipette for compositing samples can be made from an ordinary 5 cc. pipette by passing through the upper stem a glass rod which at its lower end is ground to fit perfectly the lower opening of the bulb. The lower stem is removed and replaced by a delivery nozzle only 2 or 3 mm. long, into which the ground joint extends so as to leave no dead space. In the centre—or, as the case may be, in the upper part—of the bulb a hole about 3 or 4 mm. in diameter is made. In use, the valve is lifted and the instrument is plunged quickly far below the surface of the bromine. The air escapes from the side opening, and the filling is very rapid. The pipette is now closed by

depressing the rod, and is raised above the liquid for a few seconds. It thus drains on the outside while inside the bottle. It is now quickly lifted and permitted to empty partially, or wholly, either into the chilled container used for compositing, or into the weighed glass-stoppered flask containing potassium iodide solution. For the latter purpose a pipette of similar construction but smaller size is preferable. The Lunge-Rey and other forms of weighing pipettes have also been used for this purpose in this laboratory with success. Their disadvantage is that it has proved to be impossible to get stopcocks so perfectly ground on these instruments as to hinder the escape of more or less bromine into the balance case. If used, graphite is the only permissible lubricant. It is impossible to entirely avoid loss of chlorine during the manipulations, even with every precaution. Since this loss does not by any means increase in proportion to the weight of bromine taken, it follows that a relatively large amount should be weighed, and the solution at a subsequent stage subdivided for analysis, if the quantity of chlorine present is too large for direct titration.

The Process.—Introduce about 3 grms. of the bromine, accurately weighed, or more if the chlorine content is below 0·5 per cent, into a solution of 2 grms. of potassium iodide in 50 cc. of water contained in an Erlenmeyer flask with a well-ground stopper. In warm weather, flask and contents should be previously cooled in ice. Quickly insert the stopper, and shake. Transfer to a 400 cc. Kjeldahl flask, disregarding the escape of vapours of iodine and bromine, and, after rinsing add 60 cc. of fifth normal potassium iodate (or 12 cc. of the normal solution), 24 cc. of nitric acid, and water to make about 250 cc. Proceed from this point precisely as in the analysis of a bromide (see above). Of course, when the solution is ready for titration, an aliquot part should be taken if the amount of chlorine is so large as to make this step desirable.

The bromine may for many practical purposes be determined sufficiently well by difference, since the total quantity of impurities other than chlorine is usually much less than 1 per cent.

If accuracy is desired, the total free bromine and chlorine should be determined by an iodometric titration, the weighed substance being dissolved in a considerable excess of potassium iodide solution, and the liberated iodine titrated after feeble acidification. Correcting the volume of thiosulphate here required by that equivalent to the chlorine found, the difference gives the free bromine.

It is obvious that the accuracy of the method described for the determination of chlorine in bromine, or of any other process for this purpose, cannot be shown by analyses of known mixtures, since the errors in preparing such a mixture must far exceed the analytical errors. It is only possible to show the agreement of duplicate analyses and the concordance of the analytical results with physical properties. The latter will be taken up in another paper.

As illustrative of the former, I take at random several analyses out of a large number made by Dr. H. A. Carlton.

Sample.					
6706	Found per cent of Cl	2·445	2·380		
6806	,, ,,	2·069	2·072	2·052	2·32
1220 dry	,, ,,	4·439	4·422		
1220 saturated with water		4·407	4·401		
1220 dried again		4·438	4·461		
5406		8·55	8·57		
424		5·00	4·98	5·04	5·06

It is confidently believed that the methods here described for the determination of chlorine in bromine and bromides are a practical solution of this old analytical problem, suitable for routine analyses of either technical or scientific character, and adapted to replace the indirect methods.

It is a pleasant duty here to express my obligations to Dr. Carlton for his able assistance in the work.—*Journal of the American Chemical Society*, xxix., No. 3.

NOTICES OF BOOKS.

Annual Report of the Minister of Mines for the Year ending December 31st, 1906. Victoria, B.C. : Richard Wolfenden. 1907.

This volume contains the Annual Report of the Provincial Mineralogist, Mr. W. F. Robertson, upon the mining industry in the province of British Columbia for last year, and gives tables showing the total mineral output and the actual mineral production. For purposes of comparison, summaries of the productions of the last four years are also included. The curves showing the value of the total production, lode mines, and coal and coke make it easy to form an accurate idea of the progress of the industry, while the detailed and excellently illustrated accounts of the mining operations of the various districts of the province are drawn up in such a way as to provide the maximum of reliable information.

Post's Chemisch-Technische Analyse. ("Post's Technical Chemical Analysis") Vol. I., Part III., and Vol. II., Part II. Third Edition. Edited by Prof. Bernhard Neumann. Braunschweig : Friedrich Vieweg und Sohn. 1907.

The third part of Volume III. of the third edition of this excellent treatise on analytical chemistry gives concise accounts of the most reliable and convenient laboratory methods of estimating iron, written by Prof. Lebedur, and other metals, by the general editor. The methods chosen for description include only those which give satisfactory results, and the experimental details are given in full, so that the student should find no difficulty in performing analyses with little or no help from the teacher. Electrolytic processes are included, and a short section is added upon the determination of some important metallic salts. Volume II., Part II., deals equally efficiently with the carbohydrates, alcoholic beverages, yeast and vinegar, and allied products.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 11, September 9, 1907.

Alloys of Cobalt and Tin.—F. Ducelliez.—The following table gives a *résumé* of the results of the author's work upon alloys of cobalt and tin :—

Percentage of tin.	Composition of alloys.	Definite alloys isolated.	Physical properties.	
0	Co and Co_3Sn		Brittleness increases.	Magnetic alloys.
57·65	Co_3Sn_2 and CoSn	Co_3Sn_2	D = 8·862, limit of magnetism.	
66·77		CoSn	Very brittle. D = 8·950.	Non-magnetic alloys.
85	CoSn and Sn		Becoming less hard & brittle.	
100			Malleable alloys.	

MEETINGS FOR THE WEEK.

Wednesday, 16th.—Microscopical, 8. "A New Prismatic Microscope Ocular" and "On Ghost Images seen in the Secondaries of *Coscinodiscus asteromphalus*," A. A. C. E. Merlin. "Systematic Exposure with Transmitted Light in Photomicrography," by A. Letherby.

Friday, 18th.—Chemical, 9. (Extra Meeting). Prof. Emil Fischer, F.R.S., will deliver the Faraday Lecture, entitled "Organic Synthesis and its Relation to Biology."

THE CHEMICAL NEWS.

Vol. XCVI., No. 2499.

VULCANISATION TESTS WITH PLANTATION RUBBER.

(Second Communication).

By CLAYTON BEADLE and HENRY P. STEVENS.

In a previous paper which appeared in the Chemical News (vol. xcvi., p. 37) we published the results of a number of vulcanisation tests with plantation rubbers. These experiments were carried out with a view to ascertaining the value to the manufacturer of plantation rubber as compared with the ordinary brands on the market. For this purpose we not only vulcanised and tested samples of plantation rubber, but the results we obtained were compared with similar tests made on the standard rubber, viz., hard-cure para, which was washed, dried, and subsequently vulcanised alongside of the plantation rubber.

The results of our tests showed that the plantation rubber experimented with gave better figures than the hard-cure para.

These researches have aroused considerable interest among planters, manufacturers, and others, and certain criticisms were offered in a recent issue of the *Indiarubber Journal* (Sept. 9, 1907, p. 321), to the effect that the hard-cure para was subjected by us to a more severe treatment in the process of washing than would have been the case in a rubber works, and that in consequence the nerve of the rubber had been gravely affected, while, on the other hand, the plantation rubber was not washed, but mixed straight away and vulcanised, and was therefore treated under more favourable conditions, and consequently, as might have been expected, yielded better results.

As we have since pointed out, however, it is obvious that, on a manufacturing scale, it would be necessary to wash and dry the hard-cure, and our results are all the more practical for the reason that we followed the manufacturers' example; but as properly prepared plantation rubber should not require this treatment in the factory we did not subject it to such treatment in the laboratory. Hence any disadvantages attaching to the treatment of the hard-cure in our experiments would also apply in practice, nor do we think that such treatment was more severe in our tests than it would have been on a manufacturing scale.

Since our previous communication we have been steadily at work accumulating vulcanising data, and we have now concluded a series of vulcanising tests with hard-cure which had been washed and dried by a manufacturer, and was therefore in the exact condition in which it would be used by the manufacturer himself. In this way we were able to meet the criticism above referred to, and to eliminate any disturbing influence due to the use of laboratory apparatus for washing the hard-cure.

Table I. gives the analysis of hard-cure para washed and dried as supplied by a manufacturer, and for purposes of comparison we have placed alongside a recent analysis of plantation rubber.

Table I.

	Hard-cure para, after washing and drying by manufacturer.	Plantation rubber as received by manufacturer.
Moisture	0·5	0·6
Protein	2·0	1·3
Resin	2·9	3·9
Ash	0·6	0·3
Caoutchouc (by diff.)..	94·0	93·9

The results of this series of tests are given in Table II., and, so far from proving superior to vulcanised plantation rubber, the hard-cure washed and dried by the manufacturer yielded lower figures for tensile strength than the hard-cure which we had washed and dried in our own laboratories.

Table II.

Vulcanisation reference number.		Tensile strength, in grms.	Elongation at rupture when original =1·0.	Elongation under a strain 1500 grms. when original =1·0.
203		1500	—	—
209		2046	14·4	14·3
205		2174	15·4	13·6
216	Q2	2121	13·8	12·8
265		2391	12·8	11·9
251		2682	13·9	12·2
207		2558	13·6	11·8
210		1977	13·4	—
214		2168	13·6	13·0
227		2675	13·7	11·5
225	S2	2808	13·7	10·7
250		2793	13·5	12·5
259		2872	13·5	10·9
256		2777	13·0	9·8
229	W2	2116	13·7	12·1
233		2531	13·8	12·8
270		2315	13·5	13·3 (*a*)
266	D3	2696	12·8	11·3 (*b*)
260		2886	13·2	11·4 (*c*)
257		2229	11·9	10·9 (*d*)

Duration of vulcanisation: (*a*) Three hours, (*b*) four hours, (*c*) five hours, (*d*) six hours.

These vulcanisations and tests were carried out as described in our previous communication. The letters referring to mixings and the numbers to vulcanisations. In the individual vulcanisations the time and temperature (or pressure) in the vulcanisation tests were varied so as to bring out the best results possible with each mixing. We give the results of all the vulcanisations made with these mixings, including those which yielded unsatisfactory results, as in a certain number of cases the samples were either somewhat over or under cured. But taking, in this way, a wide range of temperatures and curing for various periods, we gradually worked up from under-cured samples to those which were fully cured, finally carrying the series of tests to a point where the samples were obviously over-cured.

These vulcanisations include both long cures at comparatively low temperatures, as well as shorter cures at higher ones, and it is not therefore possible in most cases to arrange the samples in the order of the cure. However, in vulcanisations D3 the temperature in all cases was the same, the time only being varied. We are therefore able to note the progressive effect of the cure on the properties of the vulcanised rubber.

The results obtained are instructive: D3 270 heated for three hours is obviously under-cured, the cure being insufficient to bring out the full tensile strength, and the sample is somewhat "soft," showing an elongation of 13·3 with a load of 1500 grms. Vulcanisation for two hours longer is sufficient to develop the highest tensile strength obtained, the elongation with a load of 1500 grms. being 11·4. On vulcanising for six hours the sample is over-cured, the tensile strength falls again, at the same time the product gets somewhat short or brittle and the elongation (10·9) is less than in the other cases. On averaging up the tensile strength of those samples in which the conditions of vulcanisation have brought out the greatest tensile strength, it is apparent that the resulting figures obtained are much lower than those obtained in the previous tests on vulcanised hard-cure para, which had been carefully washed and dried by ourselves, and of course are considerably lower than those obtained with the vulcanised plantation rubber.

We are extending our researches on the vulcanising qualities of crude rubbers in other directions, and are at present engaged in instituting a comparison between the different forms of plantation rubbers at present on the market with a view of ascertaining which form—that is to say, whether sheet, biscuit, block, crepe, &c.—yields the strongest and most resilient product on vulcanisation.

So far as we have gone, the results obtained with different forms of plantation rubber differ materially from one another, and it would appear that in future, when this difference in behaviour is better recognised, planters will require to consider carefully whether the form in which they are shipping their rubber is that which yields the best results to the manufacturer.

ON THE CALCULATION OF THERMO-CHEMICAL CONSTANTS.

By H. STANLEY REDGROVE, F.C.S.

Molecular Heats of Formation of the Hydrocarbons.

The author has already shown that his method of calculation may be applied with great accuracy to the molecular heats of combustion of the hydrocarbons (Chemical News, xcv., 301).

The following paper deals with molecular heats of formation.

The constants that were found necessary in the consideration of physico-chemical properties in general, and defined (Chemical News, xcv., 193), can be used here; but as they will have different specific significations from that with which they were employed in the consideration of molecular heats of combustion, it will be advisable to dash them when employed in the consideration of molecular heats of formation in order to avoid confusion.

Consider the case of the general hydrocarbon :—

$$n\mathrm{C}+2(n+1-a-2b-p)\mathrm{H}+(n+p-a-b-1)\mathrm{L}_1+a\mathrm{L}_2+6\mathrm{L}_3.$$

The heat of formation of 1 molecule of this hydrocarbon from carbon molecules and hydrogen molecules is the algebraic sum of the following heats :—

1. The heat due to the dissociation of a sufficient number of carbon molecules to provide n isolated carbon atoms.
2. The heat due to the dissociation of $(n+1-a-2b-p)$ hydrogen molecules, H_2.
3. The heat of formation of $2(n+1-a-2b-p)$ C.H links.
4. The heat of formation of $(n+p-a-b-1)$ C.C links.
5. The heat of formation of a C=C links.
6. The heat of formation of b C≡C links.

The coefficients of Heats 2 and 3 are always in the ratio 1 : 2, therefore their algebraic sum can be considered as one constant.

Dealing with grm.-molecular weights and using the notation already adopted :—Heat 1 = $n\mathrm{C}'$ cals. Σ Heats 2 and 3 = $2(n+1-a-2b-p)\mathrm{H}'$ cals. Heat 4 = $(n+p-a-b-1)\mathrm{L}'_1$ cals. Heat 5 = $a\mathrm{L}'_2$ cals. Heat 6 = $b\mathrm{L}'_3$ cals.

It should be noticed that $\mathrm{L}'_1 = -\mathrm{L}_1$, $\mathrm{L}'_2 = -\mathrm{L}_2$, $\mathrm{L}'_3 = -\mathrm{L}_3$.

It has already been proved in general that the values of these constants are unobtainable at our present state of knowledge, but the values of the "fundamental constants" $\alpha'(=\mathrm{C}'+4\mathrm{H}')$, $\beta'(=2\mathrm{H}'-\mathrm{L}'_1)$, $\gamma'(=4\mathrm{H}'-\mathrm{L}'_2)$, and $\delta'(=6\mathrm{H}'-\mathrm{L}'_3)$ may be calculated in a similar manner to those for molecular heats of combustion.

In Table I A will be found the molecular heats of formation (from molecules of amorphous carbon and hydrogen molecules), corrected for constant volume, given by Thomsen ("Thermo-chemical Researches," 1906, German Edition). The values of the "fundamental constants" calculated from these results are :— $\alpha' = 21{\cdot}2$ cals., $\beta' = 15{\cdot}0$ cals., $\gamma' = 46{\cdot}0$ cals., and $\delta' = 89{\cdot}5$ cals. (see Note).

[Note.—The fundamental heat of formation constants may be more readily calculated from the heat of combustion constants as follows :—

C' = Heat combustion 12 grms. amorphous carbon at constant volume − C.

$\therefore$ $\mathrm{C}' = 97{\cdot}0$ cals. − C.

$2\mathrm{H}'$ = Heat combustion 2 grms. hydrogen at constant volume − 2H.

$\therefore$ $2\mathrm{H}' = 67{\cdot}5$ cals. − 2H.

$\therefore$ $\alpha' = \mathrm{C}'+4\mathrm{H}' = 97{\cdot}0$ cals. + 2(67·5) cals. − (C + 4H) $= 232{\cdot}0$ cals. − $\alpha = (232{\cdot}0 - 210{\cdot}8)$ cals. $= 21{\cdot}2$ cals.

Also, $\mathrm{L}'_1 = -\mathrm{L}_1$, $\mathrm{L}'_2 = -\mathrm{L}_2$, $\mathrm{L}'_3 = -\mathrm{L}_3$.

$\therefore$ $\beta' = 2\mathrm{H}'-\mathrm{L}'_1 = 67{\cdot}5$ cals. $-(2\mathrm{H}-\mathrm{L}_1) = 67{\cdot}5$ cals. $-\beta = (67{\cdot}5 - 52{\cdot}5)$ cals. $= 15{\cdot}0$ cals.

Similarly for γ' and δ'].

The molecular heats of formation of the hydrocarbons have been calculated from these values, and are given in the table. The identical conclusions can be deduced from a consideration of these as were deduced from a consideration of molecular heats of combustion. Thus, $\mathrm{T}_2 = \mathrm{L}_2 - 2\mathrm{L}_1 = 2\mathrm{L}'_1 - \mathrm{L}'_2 = \gamma' - 2\beta' = 16{\cdot}0$ cals. (the value found before), &c.

The molecular heats of formation, however, being in general much smaller quantities numerically than the corresponding molecular heats of combustion, the percentage error in calculating the former is necessarily much larger than in calculating the latter. The actual errors are of the same magnitude in each case, the only considerable one being in the case of di-isopropyl as before.

In conclusion, it would not be inappropriate to refer to Mr. Thomlinson's alleged thermo-chemical equivalents.

In calculating his constants for C and H (Chemical News, xciii., 37) from which the others are derived, Mr. Thomlinson treats CH_4 as if it could be regarded as made up of two factors, whereas it is made up of three; either Mr. Thomlinson has assumed the value of the C.H link to be zero, or else he employs his H constant to mean the algebraic sum of the heat of dissociation of ½ grm. molecular weight hydrogen, and the heat of formation of the corresponding number of C—H links in a similar manner as myself, but in this latter case the H constant is only applicable to hydrogen combined with carbon (to which I have confined myself), whereas Mr. Thomlinson uses it in general.

A further assumption is made when we come to ethane, for here the value of the C.C link is also supposed to be zero.

These assumptions I have already pointed out to be quite unjustifiable.

Mr. Thomlinson would doubtless reply that he was justified in making these assumptions, because the value of propane calculated from his figures is correct. That this fact does not confirm his assumptions is evident at once from a consideration of indeterminate equations.

To simplify matters we will consider for the time being only the hydrocarbons, so that the treatment of CH_4 as if it depended on two factors only is allowable. We then have two equations, $\mathrm{C}'+4\mathrm{H}' = 21{\cdot}750$, $2\mathrm{C}'+6\mathrm{H}'+\mathrm{L}'_1 = 28{\cdot}560$ (I use Mr. Thomlinson's figures, which are uncorrected).

$3\mathrm{C}'+8\mathrm{H}'+2\mathrm{L}'_1 = 35{\cdot}110$* is not another independent equation, because it can be derived from the first two :— $3\mathrm{C}'+8\mathrm{H}'+2\mathrm{L}'_1 = 2(2\mathrm{C}'+6\mathrm{H}'+\mathrm{L}'_1)-(\mathrm{C}'+4\mathrm{H}')$. But two equations involving three unknowns are indeterminate; now the property of such a set of eqations is such that, whatever value I choose to give to one unknown, I can always find values for the other unknowns to satisfy all the equations. Mr. Thomlinson chooses to assume $\mathrm{L}'_1 = 0$; with equal justification I could assume it to be any number; to give an actual example I will assume $\mathrm{L}'_1 = 100$.

Then, $\mathrm{C}'+4\mathrm{H}' = 21{\cdot}750$, $2\mathrm{C}'+6\mathrm{H}'+100 = 28{\cdot}560$, whence solving simultaneously $\mathrm{C}' = -208{\cdot}130$, $\mathrm{H}' = 57{\cdot}470$.

Using Mr. Thomlinson's method of "confirmation" we get $3\mathrm{C}'+8\mathrm{H}'+2\mathrm{L}'_1 = 35{\cdot}370$ (*) as on his assumption.

* In Mr. Thomlinson's paper the decimal point has been shifted, I suppose by a printer's error.

TABLE I.A.—*Hydrocarbons.*

1. Hydrocarbon.	2. Formulæ.	3.	4. M H F. (constant volume). Thomsen. Cals.	5. M.H.F. calculated. Cals.	6. Difference between Cols. 4 and 5. Cals.
Methane	$C'+4H'$	a'	+21·2	+21·2	0·0
Ethane	$2C'+6H'+L'_1$	$2_1'-\beta$	27·4	27·4	0·0
Propane	$3C'+8H'+2L'_1$	$3a'-2\beta$	33·4	33·6	+0·2
Trimethylmethane	$4C'+10H'+3L'_1$	$4a'-3\beta$	40·1	39·8	−0·3
Tetramethylmethane	$5C'+12H'+4L'_1$	$5a'-4\beta$	45·0	46·0	+1·0
Di-isopropyl	$6C'+14H'+5L'_1$	$6a'-5\beta$	57·6	52·2	−5·4
Ethylene	$2C'+4H'+L'_2$	$2_1'-\gamma$	−3·3	−3·6	−0·3
Propylene	$3C'+6H'+L'_1+L'_2$	$3a'-\beta-\gamma$	+2·1	+2·6	+0·5
Trimethylene	(*c*) $3C'+6H'+L'_1-T$	(*c*) $3a'-3\beta'-T$	−4·6	−4·5	+0·1
iso-Butylene	$4C'+8H'+2L'_1+L'_2$	$4a'-2\beta-\gamma$	+8·9	+8·8	−0·1
iso-Amylene	$5C'+10H'+3L'_1+L'_2$	$5a'-3\beta-\gamma$	16·7	15·0	−1·7
Diallyl	$6C'+10H'+3L'_1+2L'_2$	$6a'-3\beta-2\gamma$	−11·6	−9·8	+1·8
Acetylene	$2C'+2H'+L'_3$	$2a'-\delta$	−47·8	−47·1	+0·7
Allylene	$3C'+4H'+L'_1+L'_3$	$3a'-\beta-\delta$	−40·5	−40·9	−0·4
Dipropargyl	$6C'+6H'+3L'_1+2L'_3$	$6a'-3\beta-2\delta$	−97·2	−96·8	+0·4
Benzene	(*a*) $6C'+6H'+3L'_1+3L'_2$	$6a'-3\beta'-3\gamma'$	−13·7	−55·8	−42·1
	(*b*) $6C'+6H'+9L'_1$	$6_1'-9\beta'$		−7·8	+5·9
Toluene	(*a*) $7C'+8H'+4L'_1+3L'_2$	$7a'-4\beta'-3\gamma'$	−5·3	−49·6	−44·3
	(*b*) $7C'+8H'+10L'_1$	$7a'-10\beta'$		−1·6	+3·7
Mesitylene	(*a*) $9C'+12H'+6L'_1+3L'_2$	$9a'-6\beta'-3\gamma'$	−2·4	−37·2	−34·8
	(*b*) $9C'+12H'+12L'_1$	$9a'-12\beta'$		+10·8	+13·2
Pseudocumene	(*a*) $9C'+12H'+6L'_1+3L'_2$	$9a'-6\beta'-3\gamma'$	−1·6	−37·2	−35·6
	(*b*) $9C'+12H'+12L'_1$	$9_1'-12\beta'$		+10·8	+12·4

(*a*) Kekulé's formulæ.

(*b*) Ladenburg's or Claus's formulæ, without subtracting the value due to tension; in the case of Ladenburg's the value of this intramolecular tension is greater than 46·2 cals.

(*c*) T is the thermal value of the intramolecular tension in the trimethylene molecule, and has been found to be equal to 23·1 cals. It should be borne in mind that whilst in calculating molecular heats of combustion this value is to be added; in calculating molecular heats of formation this value must be subtracted.

So that if Mr. Thomlinson has shown that the values are $C' = -8'130$, $H' = 7'470$, and $L'_1 = 0$; with equal logic I have shown them to be $C' = -208'130$, $H' = 57'470$, $L'_1 = 100$. This, I think, settles the question, and clearly shows that the true values are unknown and indeterminate.

This is only a particular case of the general proof I have given (CHEMICAL NEWS, xcv., 193).

It should also be noticed that Mr. Thomlinson has to make a very large number of assumptions, without any justification, to bolster up his hypotheses. Thus we have such weird formulæ proposed as O≡O and $(OH)_3P$—O (*i.e.*, tetravalent phosphorus and penta- and monovalent oxygen are assumed); in fact, a very loose conception of valency seems to permeate his papers.

For instance, what does this mean (CHEMICAL NEWS, xcv., 50):—"If in nitrous oxide, N_2O, oxygen be represented as pentavalent, but with the difference that in the structural formula shown below, in which nitrogen is trivalent, there is one oxygen bond of valency which forms a central union in the molecule, without affecting the trivalency of nitrogen . . . $\begin{matrix} N \\ \gtrless \\ N \end{matrix} \!\!\geqslant O$"?

It appears, when simplified, to reduce to the statement $2 = 1$!

Even with all this bolstering up, Mr. Thomlinson's calculated values are not on the whole in good agreement with the experimental results, as reference to his papers make evident.

The Polytechnic, Regent Street, W.

[NOTE.—The author's attention has recently been called to a paper by Thomsen (*Zeit. Phys. Chem.*, 1905, li., 657) in which a method of calculating the heats of combustion of hydrocarbons is employed, resembling somewhat the author's method. It is, perhaps, unnecessary to state that the short criticism in CHEMICAL NEWS (xcv., 301) did not apply to this method].

THE ARTIFICIAL REDISTRIBUTION OF THE METALS.

By H. M. ATKINSON.

ALTHOUGH man's activities are confined to a thin film of the earth's sphere, yet the total effect of these, acting as they have been for some thousands of years, must have produced a considerable effect on the distribution of the elements, the metals especially. It amounts to a redistribution, for the accumulation, *e.g.*, of the noble metals, is not a permanent one. For, leaving out of account the atomic changes which gold, &c., may undergo, these metals are subject to wear—a sort of human denudation. This takes place chiefly in civilised countries, and the result of this denudation is a diminishing of the useful or active mass of metal, and the transference of this amount to the deposit settling at the mouths of rivers, or a little beyond them. The gold, silver, &c., thus carried off must be in excessively fine particles, so small that their weight is not materially different from the particles of sand, clay, &c., carried along with them; so that a more or less homogeneous mixture would be laid down.

Thus the metal is lost; for even supposing earth movements laid bare these deposits sufficiently thick to work, the percentage of gold would be so small that it would not pay our descendants to work them, at any rate with modern processes of extraction. The noble metals then are being extracted from the ancient rocks, their chief source where their local concentration is comparatively large, and are laid down again in new rocks where their concentration will be very small.

Tin seems to offer a good illustration. Tin oxide has a large concentration in a few scattered places on the earth's surface. It is mined, reduced, and spread pretty uniformly over the world as tin sheet. Rusty old tins are an eyesore on the refuse heaps round all towns. The tin gets oxidised, and ultimately the particles are washed down into the rivers, and by them spread over the sea-bottom. Here

also a more or less uniform distribution of tin is taking place, and a lowering of the concentration.

As de Morgan said, "The second instance begins the induction." This leads me to my thesis :—

Man's effect on the distribution of the metals tends to the formation of a uniform deposit.

The older rocks contained patches or veins of great richness in some metals and absolutely devoid of others; the new rocks will be poor in all. Somewhat similar to the destiny of energy, *i.e.*, uniformity.

I do not overlook the fact that other circumstances may be at work countering this effect. The "*Erz-lagern*" have probably been formed by solution; the long infiltration of solutions, very dilute it is true, formed under the great pressures in the earth's crust. But these counter effects would not be so powerful in ocean or sea deposits when forming.

Could any experimental evidence be obtained? The difficulty in the way would be great. The mere getting of a sample for analysis, sea-mud beyond the Mersey bar, *e.g.*, would be easy enough; the analysis for minute traces of the common metallic elements would be difficult, as traces of gold have been found in sea-water itself.

There are many side issues from the main theme. Is the composition of the sea itself being altered? The effect of modern manufacturing processes might seem to indicate an accumulation of soluble chlorides; an up-to-date farmer sends a larger amount of potash and lime salts to the common sink than before; thus the Stassfurth K concentration is lowered to the marine K concentration.

THE QUANTITATIVE SYNTHESIS OF ARGENTIC NITRATE, AND THE ATOMIC WEIGHTS OF NITROGEN AND SILVER.*

By THEODORE WILLIAM RICHARDS
and
GEORGE SHANNON FORBES.

(Concluded from p. 183).

The Purity of the Fused Argentic Nitrate.

THE first impurity for which search was made was air. While crystals obtained from solution, although always containing solvent, may be supposed to be free from air, the fused material cannot without question be assumed to be free from this impurity. The only manner of approaching this question seems to be to fuse the salt a second time in a vacuum, in order to detect a possible loss of weight. This Stas did in a single case, with a negative result. Nevertheless, a single experiment, even of Stas's, does not carry with it much weight; therefore the test deserves repetition.

This was carried out in the present case without great difficulty on five of the preliminary determinations. The flasks containing the argentic nitrate which had been fused for an hour in air were lowered into mammoth test-tubes —long tubes of soft glass 4·5 cm. in diameter—sealed at the lower end and scrupulously clean. A hood was placed over the mouth of the flask to prevent fragments of glass from entering, and the tube was drawn down in two large converging blast flames. A glass tube was fused on and connected with an efficient mechanical hand-pump; several exhaustions, followed by admission of dry air, excluded all moisture. Finally, the system was reduced to 2 mm., and sealed, and heated to 210°. After having been maintained in a state of fusion in the dark for half-an-hour, the salt was cooled in the usual cautious fashion, and air was admitted very slowly. The flask was placed in a desiccator over-night, and weighed. The product was always slightly discoloured, indicating decomposition, but showed no serious loss in weight.

The Effect of Fusion in Vacuum.

Determination number.	Original weight.	Weight after fusion.	Change.
	Grms.	Grms.	
1.	8·04489	8·04477	−0·00012
2.	8·75813	8·75810	−0·00003
3.	8·54170	8·54170	0·00000
4.	9·87850	9·87837	−0·00013
9.	10·76381	10·76374	−0·00007

Forty-five grms. of salt lost in all 0·00035 grm. This is less than 1 part in 100,000, and may safely be referred to the trace of decomposition indicated by the pale brownish coloration. Not only is it reasonable to suppose that but little air is dissolved (for according to the law of Henry nearly all of it should have been expelled by this treatment), but also one is led to infer that very little water remains to be expelled. This matter is not, however, so simply settled; the final testing of it cost much labour.

It has been ordinarily assumed that water is entirely expelled from crystallised or evaporated salts upon fusion. This is in all probability the case with sodic and potassic chlorides, and other salts which fuse at high temperatures and show little affinity for water. Whether or not this was the case with argentic nitrate, which at 210° is miscible with water in all proportions, was a question which required experimental investigation.

Besides the conservation of weight on fusion in a vacuum another argument may be adduced to show that most of the water has been driven out. The combining weight of argentic nitrate seems to be nearly independent of the time of its fusion in a current of dry air, as is shown by the following table :—

Determination.	Time kept in fusion.	Weight of $AgNO_3$ formed from 100 parts Ag.
14	15 minutes	157·481
9, 10, 11, 12, 13	1 hour	157·480
15	3 hours	157·480

It should be stated that the last residue was slightly discoloured, and increased 0·00008 grm. upon a subsequent evaporation with water and nitric acid; hence a real loss of weight during the extra period of fusion is indicated; but this was probably due to decomposition of the salt rather than to escape of water; therefore the table bears out the contention stated above. In any case this loss amounts to much less than a unit in the last decimal place.

Ordinarily, in the past, the investigator has been satisfied with such an outcome, and has gone no further. But in this case we were anxious to leave no stone unturned, and accordingly a drastic method of treatment was adopted, which permitted no trace of water to escape being weighed. This was to decompose completely the argentic nitrate by heat, and to pass the gaseous product of the decomposition through a weighed tube containing phosphoric oxide.

A hard glass combustion tube was bent and drawn out in the manner shown in Fig. 2, the space between C and D being packed with glass-wool. Into the space between B and C was then introduced about 50 grms. of argentic nitrate which had been crystallised from nitric acid, barely fused in porcelain, cooled, and pounded in a mortar. The tube was heated to 220° in an air-bath for an hour in a stream of dry air passed in through A. The argentic nitrate should now be in a condition somewhat comparable to that of the quantitative determination. Finally, a weighed pentoxide tube was attached at D, and the temperature raised to 500°. Yellow oxides of nitrogen came over, also a fine grey dust caused presumably by the bursting of bubbles of decomposing salt. After an hour the pentoxide tube was removed, swept out with air, and weighed again. A trace of the grey dust had been carried in, and suggested a slight gain in weight, but by no means enough to account for the great increase of weight, 0·012

* *Publication* No. 69, Carnegie Institution of Washington.

grm. This was finally traced to the adsorption of nitrous fumes by the pentoxide, 2 mgrms. being lost upon passing dry air over the tube for an hour, and the rest giving a very strong test for nitrous acid after being dissolved in water.

In the effort to eliminate this seriously disturbing effect, recourse was next had to spirals of copper gauze heated in a combustion tube, in order to abstract the oxygen from the nitric oxide, leaving only nitrogen. It is well known that metallic copper adsorbs hydrogen ; hence the spirals were first superficially oxidised in a stream of dry air, and then reduced by pure dry carbon monoxide. This was generated by heating the purest oxalic and sulphuric acids of commerce together, the carbon dioxide being absorbed by a generous train of pure concentrated potash solution, and the monoxide dried first by a tower of concentrated sulphuric acid, with beads, and finally by two towers of pounded potash. The resulting copper should be above the suspicion of containing any considerable amount of hydrogen or moisture. The argentic nitrate was treated as before, and the decomposition was continued until traces of yellow fumes were noted coming past the copper. This meant that nitric oxide had been coming over for some time, since the last part of oxygen is harder to detach than the first. When swept out with air, the gas in the pentoxide tube turned yellow, but it was not then supposed that much nitric oxide could be absorbed by the pentoxide in so short a time. Nevertheless, nitrous acid was found upon solution, even although the gain in weight was only a third as great as before.

Fig. 2.—Tube for Decomposition of Argentic Nitrate. (About one-eighth actual size).

Efforts were now made to reduce accidental water from rubber, &c. All joints were made to overlap, so that the rubber surfaces exposed to nitric oxide might be small, and large asbestos screens kept them from being overheated by the adjacent furnaces. Fresh sublimed pentoxide was used in the weighing-tube, which was carefully imitated as to volume and surface by a similar tube, to be used as a counterpoise in weighing ; both were opened after coming to the temperature of the balance-room, wiped with a clean slightly damp cloth, and weighed by substitution. A substantial plug of glass-wool in the decomposition tube strained the gases before passing over the copper ; it had been heated in the dry air to remove moisture.

To eliminate the possibility of water in the copper gauze and to test the apparatus, a blank run was made, removing the decomposition tube, and oxidising the copper with dry air. Here the pentoxide tube lost 0·0004 grm., a result which indicated no error in that part of the process.

It is not worth while to record the individual experiments by which the gradual improvements in apparatus and manipulation were tested, tiresome and time-consuming as these were in execution. By the time seven experiments had been performed, it was clear that the fused argentic nitrate could not contain over 0·004 per cent of water. Even of this small amount a part was undoubtedly due to nitric peroxide ; for the copper gauze was not enough to effect a complete decomposition of the gases. Passing carbon monoxide through the apparatus while the decomposition was in progress lengthened the effective life of the reduced copper, but introduced other complications, and the addition of a second tube of hot gauze, a metre long, was still inadequate.

The next step was to secure a copper surface so large that all the nitrogen oxide resulting from the complete decomposition of 50 grms. of argentic nitrate could be removed, and this without increasing the complications of the apparatus. Powdered copper oxide looked promising as a source of this metal, but it must be made from pure materials to avoid the presence of detrimental impurities. Pure electrolytic copper (Merck) was dissolved in nitric acid, evaporated to dryness in porcelain, and very gradually ignited with constant stirring, to powdery oxide. A hard glass tube 30 cm. long and 3 cm. internal diameter was used to contain it ; the ends were drawn down conveniently, and the oxide was reduced at a very moderate heat with carbon monoxide, prepared as usual, except that it was finally dried with pentoxide. Nearly 300 grms. of copper oxide were present ; therefore the process was very tedious, since the gas had to pass through its purifying train at a moderate rate of speed. With this large mass of finely divided copper the glass-wool (from C to D in the diagram) was no longer necessary, therefore it was no longer used. No trace of powdered nitrate ever appeared beyond the copper.

A clean pentoxide tube, with glass stopcocks, was refilled with re-sublimed pentoxide and glass-wool ; dry air was passed through for ten minutes to assure constancy. A duplicate tube was also prepared for a counterpoise, and extraordinary precautions were taken in protecting and weighing these tubes. As another precaution it seemed also expedient to prepare argentic nitrate nearly as pure as that used in the determinations for fear of hygroscopic nitrates, silicic acid, and ammonium salts, which would yield water when decomposed. A moderately pure salt was re-crystallised from nitric acid, filtered, precipitated with formate, washed free from ammonium salts, and fused on lime in the blast. The buttons were etched, and dissolved in freshly distilled nitric acid in Jena glass, and the salt was crystallised with ample protection against ammonia, dried centrifugally, and kept in a clean tight desiccator. There was no ammonia in this product. Before using it was fused in platinum.

In the first determination of this series the argentic nitrate was heated too hot (520°), and the gases came over so fast that the reduced copper was only superficially attacked ; even so it was vastly more efficient than the gauze. Because, however, some nitric peroxide still escaped, this experiment also had to be rejected, a part of the 0·004 per cent impurity which it indicated being undoubtedly due to nitrous fumes.

The apparatus was now improved by sealing off the end (A) of the tube after the argentic nitrate had been fused for a long time in a current of dry air. Moreover, the last trace of rubber exposed to nitrous fumes was eliminated by providing an accurately ground joint between the decomposition tube and the copper oxide. The process was conducted so slowly at 490° that the argentic nitrate could be entirely decomposed to pure spongy silver without exhausting all the copper. Care was taken to have the very pure argentic nitrate in a state comparable to that used in the determinations. The salt after its preliminary treatment in platinum still contained a few crystals of unfused nitrate ; accordingly, in the tube it was heated evenly at 220° with shaking to dislodge steam bubbles, exactly as the determinations had been. Under these conditions reliable results were obtained. In No. 25, a second weighed pentoxide tube placed in tandem with the first showed no gain in weight ; hence the first tube caught all the water-vapour. The remaining nitrogen was driven out by pure dry air before weighing. That water-vapour was actually present was shown by the "melting" of phosphoric pentoxide in the first tube.

Water obtained by Decomposition of Argentic Nitrate.

Experiment number.	Weight of $AgNO_3$ Grms.	Gain in weight of drying tubes. Grm.	Percentage of water found.
25	53	0·0015	0·0028
26	52	0·0011	0·0020
27	44	0·0014	0·0033
Average ..	50	0·0013	0·0027

Thus it is clear that less than 0·003 per cent of water was

held by the argentic nitrate after fusion. There was only one other source from which this mgrm. or so of water might have come, namely, from the copper used for the reduction of the nitrous fumes. Less than 0·0002 grm. of hydrogen retained by 300 grms. of copper, or less than one part in a million, would have been enough to cause this effect; hence it seemed rash to assume that the water did not come from this source. As much hydrogen as this might have come from a trace of moisture in the hundred litres of carbon monoxide used for the reduction of the copper.

The question thus raised was capable of being investigated. For this purpose the mass of copper, reduced just as it would have been for one of the preceding experiments, was twice oxidised by a very large volume of pure ignited air dried with the usual potash towers, and finally with phosphoric pentoxide. This air, having been already passed over red-hot cupric oxide in a hard glass tube and thoroughly dried by pentoxide, could hardly bring with it any water which could be taken up by the following tube of the same material. On one of these occasions, 0·0009 grm. of water was found, and on another 0·0007 grm. Possibly some of this may have come from the atmosphere during the manipulation of the tubes, but a similar amount must be supposed to have been taken during each of the previous determinations. Hence it seems to be permissible to subtract the average 0·0008 grm. from the average result of Experiments 25, 26, and 27, namely, 0·0013 grm. This leaves only 0·0005 grm. as the maximum amount of water held by 50 grms. of carefully fused argentic nitrate, introducing an error of only 1 part in 100,000. As the average of the final series led to a value a trifle over 157·480 grms. as the weight of nitrate obtainable from 100·000 grms. of silver, the correction to be applied for water reduces the result only to 157·479. Possibly not even as much water as this was present in the quantitatively made argentic nitrate, because the relative surface exposed for drying was not so great in the long narrow tube just used as it was in the quartz flask employed for Experiments 10 to 15,

This unimportant change in the synthetic result from 157·480 to 157·479 was the only apparent outcome of these tedious and often exasperating experiments on the decomposition of the nitrate, but in reality more was shown by them. The experience furnished to the experimenters a striking example of the essential importance of taking as much care in determining a small correction as in determining the quantity to be corrected. It, moreover, confirmed the impression that, except in cases like the chloride of zinc, when water acts chemically upon the substance, little or no water is retained by most fused salts. If argentic nitrate, which at 200° is miscible with water in all proportions, sets free so nearly all that it possesses in a current of dry air at this temperature, it is much more likely that other salts, fusing at a higher temperature and possessing a less attraction for water, should be free from it after fusion. This is a reassuring conviction, well worth the trouble spent upon the point.

Attention was now directed to other foreign substances besides water and air which might be present in the synthetic argentic nitrate. Further careful investigation was needed to show that all the silver was combined as nitrate, and that no other impurities were concealed in the salt. The pure pearly whiteness of the cold fused material precluded the possibility of there having been a trace of reduction to metallic silver. The salt was soluble in pure water without residue or turbidity, and maintained its clearness when diluted to half or quarter normal; hence oxide and halogen salts must have been absent. The only other likely impurity seemed to be ammonium salts, nitrite, and excess of nitric acid. Of these possibilities, Stas thought only of the likelihood of the presence of free acid, but each was carefully considered in the present work.

It is known that copper dissolving in nitric acid forms perceptible quantities of ammonic nitrate. Apparently, no similar reaction has been noted with silver, and from an electro-chemical standpoint it seemed unlikely; moreover, ammonic nitrate, if present, would probably be for the most part decomposed by the hour's fusion of the silver salt. Nevertheless, thoroughness demanded evidence on this point. Nessler solution is the most convenient for this test, but silver must first be precipitated from solution in the dark. Light generates chlorine which interferes with the test.

In order to prepare for this search for ammonia, the synthetic nitrate of silver resulting from several experiments was shaken with a slight excess of standard pure sodic chloride until the supernatant liquid was clear; the latter was decanted, made up to 50 cc., and placed in a comparison cylinder. The sodic chloride gave no test with Nessler solution.

The cylinder full of liquid prepared from the argentic nitrate was finally tested by comparison with other cylinders containing known traces of ammonic nitrate mixed with sodic nitrate in concentration equal to that existing in the actual determination. The sodic nitrate had been several times re-crystallised with centrifugal draining, and was shown to be free from ammonia. In this way the following results were attained:—Synthesis 12 was found to contain 0·05 mgrm. of ammonic nitrate, Synthesis 13, 0·06 mgrm., and Synthesis 14, 0·05 mgrm.; in all, 36·5 grms. of argentic nitrate were proved to contain no more than 0·00016 grm. of ammonic nitrate—less than one two-thousandth of 1 per cent. The source of this ammonia was not determined; it might have come from the reduction of nitric acid or from the large volume of air used in evaporating the argentic nitrate. The only possible place where it could have entered with the reagents used in the test was in the sodic chloride solution; this was indeed tested, with negative results, but Nessler's reagent is not very sensitive in the presence of chloride, and a trace of ammonia might have eluded detection. If the amount found had been larger, more time would have been spent upon the matter, and a sample of the argentic nitrate often re-crystallised in an atmosphere free from ammonia would have been used in a blank experiment for comparison; but with such a small trace of impurity this was not worth while.

In summing up the results of the test for ammonia, the amount should be calculated for the quantity of argentic nitrate produced from 100·000 grms. of silver. Thus it is found that 157·480 grms. of fused argentic nitrate could not have contained over 0·0007 grm. of ammonic nitrate.

The next impurity to be studied, nitrous acid, was sought by means of sulphanilic acid and naphthylamine hydrochloride. These were proved with a standard nitrite solution of which 1 litre contained 0·1 grm. of nitrogen. To insure parallel conditions in testing by comparison, pure silver nitrate was prepared with some care. It was thrice re-crystallised from nitric acid with centrifugal treatment, fused in porcelain, then re-crystallised three times more from the purest water in platinum, with centrifugal draining as before. The specimens of fused argentic nitrate resulting from quantitative determinations were dissolved in known amounts of water, and comparison solutions of equal concentration prepared. The crystallised silver nitrate gave no trace of pink colour with the reagents. A fresh solution to which 0·1 cc. of nitrite solution (0·01 mgrm.) had been added gave a pronounced colour, while Determinations 2, 3, and 11 all gave a much fainter barely visible colour; hence it was permissible to conclude that the loss of oxygen from the nitrate on fusion could not have exceeded 0·000005 grm., a wholly negligible quantity.

In seeking for the next impurity, free nitric acid, Stas tested aqueous solutions of his fused silver nitrate with "tournesol," and found them alkaline rather than acid. This alkali may have come from his glass vessels. We used methyl-orange, a more sensitive indicator, and noted that the purest crystallised neutral specimens and the fused salt alike gave equally pronounced acid reactions in solu-

tion. The colour was not modified by the addition of half a mgrm. of nitric acid; therefore the equality in colour does not disprove the presence of free acid in our fused product. Dilute sodic hydroxide freed from carbonate by baric hydroxide threw down a precipitate without changing the pink colour. Hence the indicator was discarded, and the investigation continued with the nephelometer.

The test for acid with the help of this instrument was conducted by adding a very dilute standard caustic alkaline solution to the solution to be tested, and by observing if this addition caused a permanent cloud.

Preliminary trials were necessary, in the first place, in order to determine the conditions best suited for accuracy. It was found that a concentration of nitrate no stronger than 4 grms. in 0·025 litre was best adapted to this work, as argentic hydroxide is distinctly soluble in double this concentration of argentic nitrate. On the other hand, argentic hydroxide precipitated by somewhat concentrated alkali does not quickly re-dissolve in an equivalent quantity of nitric acid, mixed with the dilute argentic solution. It was found that even the precipitate caused by 0·1 millilitre of a two-hundredth normal solution may produce a fairly permanent cloud in spite of the presence of an excess of 0·00003 grm. of nitric acid, enough to dissolve it. Still more dilute solutions behaved much more satisfactorily, however,. A millilitre of a two-thousandth normal caustic solution (equivalent to 0·00003 grm. of nitric acid) added with constant stirring to the pure standard argentic nitrate formed a cloud easily seen in the nephelometer. In case 0·00003 grm. of nitric acid had been introduced before adding alkali, no precipitate was formed under the same conditions. Hence under these circumstances the test attained a degree of sensitiveness suited to the case in hand.

In this way it was found that the argentic nitrate remaining from Synthesis II gave a distinct opalescence with the addition of 0·00002 grm. of sodic hydroxide, and an obvious cloud with 0·00003 grm. Hence it was concluded that argentic nitrate fused in a stream of pure air for one hour contains no weighable excess of nitric acid.

The various suspected impurities having thus been duly sought, it is instructive and interesting to tabulate the results. These are as follows:—

	Grms.
Weight of fused $AgNO_3$ from 100,000 grms. Ag	157·480
Correction for weight of—	
Dissolved air	0·000
Retained water	−0·0016
Retained ammonic nitrate	−0·0007
Nitrite	0·000
Free acid	0·000
Corrected weight of argentic nitrate obtainable from 100·000 grms. of pure silver ..	157·478

As the subtractive corrections given in the above table are maximum values, the weight of argentic nitrate in question can hardly be lower than this value, 157·478. On the other hand, it can hardly be higher than the uncorrected value, 157·480. Thus two limits are set, very near together, between which the true value must lie. Obviously, for the present one cannot go very far astray in accepting the mean value, 157·479, and this value will be used in the following discussion.

The Final Result and its Relations to the Values of Atomic Weights of Nitrogen and Silver.

The conclusion reached by the foregoing series of experiments is that 100·000 parts of silver yield very nearly 157·479 parts of argentic nitrate. Among other experimenters, Penny found 157·442; Marignac found 157·424; Stas found 157·474 in one series of seven determinations and 157·486 in another of two; and Hardin found 157·484. From these older figures, by an interesting coincidence Clarke calculated exactly the value found in the present research ("Re-calculation of the Atomic Weights," 1897, p. 64). This coincidence is to be attributed not so much to the efficacy of the method of calculation as to the fact that in this case the impurities in the silver happened to balance exactly the impurities in the argentic nitrate. At first sight it is incomprehensible how Stas, working with slightly impure silver, could have obtained any results higher than the true value; but it must be remembered that his nitrate was fused in a glass vessel, which must have been attacked by the strongly acid nitrate at 220°. Constancy in the weight of the vessel would be no evidence of absence of action, for silver might partly take in the glass the place of the sodium taken from it. Thus a gain in weight due to sodic nitrate might be accompanied with no considerable loss of weight of the vessel. In favour of this hypothesis is the fact that Stas's results steadily decreased in each series as he proceeded with the work; the flask seems to have been less and less susceptible to attack, as is reasonable. If the last two determinations of the first series are taken as the most nearly free from this cause of error, the number 157·466 obtained from them should furnish, by comparison with our number, some clue to the amount of gaseous impurity in Stas's silver. Thus it appears that his silver must have contained nearly 0·01 per cent of impurity—probably more if it is considered that the flask was still not wholly resistant—a conclusion not very different from that reached by Richards and Wells.

Speculations of this kind concerning older work are rather a thankless task, however; there is usually too much that is doubtful to allow them to serve a very valuable purpose. The only object in pursuing the review at all is in order to assure one's self that no real inconsistency exists in the data.

Attention is now directed to a more important matter, namely, the effect of the new experimental result upon the table of atomic weights. This is quickly stated:—The newly advocated low atomic weight of nitrogen is incompatible with the ratio 100·000 : 157·479, if silver is taken as 107·930. If, on the other hand, the new atomic weight of nitrogen is the true one, silver must have a much lower value than this.

The exact figures are given in the following table:—

The Atomic Weight of Nitrogen.

If Ag = 107·930, $AgNO_3$ = 169·967, and N = *14·037*
If Ag = 107·890, $AgNO_3$ = 169·904, and N = *14·014*
If Ag = 107·883, $AgNO_3$ = 169·893, and N = *14·010*
If Ag = 107·880, $AgNO_3$ = 169·888, and N = *14·008*

This series of conditional statements contains in a nutshell the result of the present investigation. In order to decide between the alternatives, other compounds must be further studied, especially the chlorates and the ammonium salts. Investigations in both of these directions have already been begun in the Chemical Laboratory of Harvard College.

Summary.

Argentic nitrate was made from pure silver, and the gain in weight was carefully noted.

In the course of the work, a new and convenient apparatus for quantitative evaporation was devised. Quartz flasks were used as a part of it.

The argentic nitrate was fused until constant in weight; it was carefully tested for dissolved air, retained water and ammonia, and nitric and nitrous acids. Only the second and third of these impurities could be detected by tests proved to be adequate, and these only in mere traces, between 0·001 and 0·002 per cent in all.

The outcome was that 100·000 parts of pure silver produced 157·479 parts of argentic nitrate. If, then, silver is taken as 107·93, nitrogen must be 14·037; or if silver is taken as 107·880, nitrogen must be 14·008, oxygen being 16·000.

ON THE ESTERIFICATION OF SUCCINIC ACID.

By I. K. PHELPS and J. L. HUBBARD.

In a former paper from the Kent Chemical Laboratory of Yale University (*Am. Journ. Sci.*, xxiii., p. 211) it has been shown that succinic acid analytically pure may be prepared from succinic ester by hydrolysis in presence of a small amount of nitric acid; and, further, that the acid prepared in this way is of a decidedly higher degree of purity than that of the so-called chemically pure acid of commerce. This paper concerns the study of certain conditions under which the preparation of the pure diethyl ester, $C_2H_4(COOC_2H_5)_2$, is readily made, and also certain conditions under which the esterification of the acid seems to be almost quantitatively complete.

The reaction for the formation of an ester from an alcohol and an acid with the elimination of water is a common example of what is termed a reversible reaction. In order to avoid reversion of the reaction, various methods of dehydration have been made use of in the processes brought out for the formation of esters. This seems to have been accomplished most successfully by Fischer and Speier (*Ber.*, 1895, xxviii., 3252), although as early as 1864 Carey Lea (*Am. Journ. Sci.* [2], xxxix., 210) showed that in the esterification of oxalic acid there is an advantage in acting upon the acid in a tube with gaseous alcohol, in comparison with the usual method of esterification by heating oxalic acid with alcohol. Fischer and Speier have shown that when 1 part by weight of acid and 3, 4, or 5 parts of absolute alcohol containing 1 or 3 per cent of hydrochloric acid are boiled on a return condenser for four hours, the product poured into cold water after distilling off half to three-quarters of the excess of alcohol, the aqueous mixture shaken out with ether, the ethereal extract dried and fractioned, gives of the ester a yield which is considered good when compared with the amount obtainable by other methods. While this procedure generally gives good yields when used for the esterification of organic acids, the esterification of each individual acid must, nevertheless, be studied by itself in detail; for, as Fischer has stated, the best yields in given cases are obtained by varying the general procedure.

In Fischer's procedure for the preparation of the ethyl ester of succinic acid the absolute alcohol is a solvent for succinic acid and its esters. It is, also, a dehydrating agent. But inasmuch as the water remains with the alcohol and the esters, it may still be active in holding back the completion of the reaction in which the normal ester is formed. Fischer's best yield was 73·9 per cent of that theoretically possible.

In the work here described the attempt has been made to reduce the proportion of water, the presence of which may retard the completion of the action, by introducing the vapour of alcohol charged with dry hydrochloric acid into the solution of succinic acid in alcohol also charged with hydrochloric acid, and allowing the alcohol, water, and hydrochloric acid to pass out from the hot solution to a condenser.

In every experiment recorded in the table, alcohol charged with dry hydrochloric acid was boiled in a 500 cc. flask fitted with a separating funnel and an outlet tube, and passed in vapour to the bottom of a 250 cc. sideneck flask containing a definite weight of succinic acid and a definite volume of alcohol charged with a definite weight of dry hydrochloric acid. The temperature of the mixture in the sideneck flask was kept between 100° and 110° by heating the flask in a bath of sulphuric acid and potassium sulphate, and this temperature was indicated by a thermometer dipping in the mixture and held in a two-bored stopper fitted to the sideneck flask and carrying also the glass tube for the introduction of the vapour (H. Scudder, *Journ. Am. Chem. Soc.*, 1903, xxv., 161). The vapour liberated in the sideneck flask passed through the sideneck to a condenser and was collected as the liquid distillate. This distillate contained whatever ester may have passed along with the hydrochloric acid, alcohol, and water mixture. As succinic ester boils at 213·3° and as the temperature in the sideneck flask was maintained between 100° and 110°, the amount of succinic ester in the distillate was necessarily a small part of the total ester produced in the reaction.

The mass of ester with its impurities from the sideneck flask was poured into a separating funnel containing a little ice, the last traces of the liquid being transferred from the flask to the funnel by successive rinsings with ether. The impure ester in the funnel was treated with an excess of dissolved sodium carbonate, and the water solution was drained off from the supernatant mixture. This mixture was washed free from sodium carbonate with a water solution of sodium chloride of sufficient density to separate it easily from the mixture. To recover any portion of the ester carried along in the water solution of sodium carbonate and the wash-water containing sodium chloride, each solution was shaken out separately three times with fresh portions of ether which were added to the main portion of the mixture. These mixtures of ester in the ethereal solutions were gathered in a 250 cc. sideneck flask connected with a 100 cc. sideneck flask as a receiver in the usual way for a vacuum distillation. The lower boiling-point impurities in the succinic ester, presumably composed chiefly of ether, alcohol, and water, were removed by allowing a gentle current of air to pass through the apparatus while the flask containing the ester solution was heated in a water-bath raised finally to 60° until the pressure registered on the manometer (15 mm.) indicated that only succinic ester remained in the flask to be distilled. The ester was then distilled over by heating the 250 cc. flask in a bath of sulphuric acid and potassium sulphate at 140—150°, and collected in the second flask, which was cooled by allowing a current of cold water to strike it constantly during distillation. The last traces of ester left on the distilling flask were removed by flaming suitably the sidewalls of the flask and at the same time increasing the current of air that was passing through the apparatus. The increase in weight of the receiver gave the weight of the succinic ester left in the sideneck flask when the acid was esterified as completely as possible under the conditions imposed in each experiment.

To recover whatever succinic ester might have been carried to the condenser with the alcohol and other vapours during esterification, the acid alcoholic distillate was chilled with ice, diluted with three or four times its volume of water, and shaken out three times in a separating funnel with fresh portions of ether. The ethereal solution thus obtained was treated with an excess of sodium carbonate in solution, washed with distilled water, and distilled *in vacuo*, in the manner described above, to separate the low boiling-point materials present, largely ether, alcohol, and water, and finally to distil the succinic ester, which was weighed.

The sources of loss inherent in this method for the preparation of pure succinic ester were carefully studied. It was found, first, that if a known weight of pure succinic ester, 75 grms., was taken in a separating funnel, shaken with sodium carbonate solution containing ice, separated from the sodium carbonate solution, washed with distilled water containing common salt, and united with the portions of ester carried on mechanically, and recovered from the water solutions by shaking out three times with fresh portions of ether, that the weight of the ester recovered on distilling *in vacuo* the ethereal solution containing some water was less than the amount taken by only 0·60 grm.

It was found, further, that when a portion of 5 grms. of succinic ester was put with 300 cc. of the alcoholic hydrochloric acid mixture used in esterification and treated exactly in the manner described for the recovery of the ester from the acid alcoholic distillate, the mass of succinic ester recovered showed a loss of only 0·50 grm.

It was found, also, that when 75 grms. of succinic ester held in a flask fitted with a receiver and capillary tube for a vacuum distillation were heated for an hour in a water-

No.	Succinic acid.	Alcohol with HCl.		Succinic ester. Theory.	Found.	Found in distillate.	Total yield.	Reaction time.	
	Grms.	Cc.	Per cent.	Grms.	Grms.	Grms.	Per cent.	Hours.	Minutes.
				A.					
1.	50	100	1·25	73·7	50·07	0·60	68·0	0	30
2.	50	100	1·25	73·7	55·06	0·00	74·9	1	25
3.	50	150	1·25	73·7	62·26	0·47	85·1	0	45
4.	50	200	1·25	73·7	66·30	0·90	91·2	1	55
5.	50	200	1·25	73·7	66·27	1·40	91·8	1	50
6.	50	250	1·25	73·7	65·60	2·15	91·9	2	25
7.	50	250	1·25	73·7	69·05	1·65	95·9	3	0
8.	50	300	1·25	73·7	67·10	3·25	95·5	4	0
9.	50	300	1·25	73·7	69·85	1·65	97·0	5	20
10.	50	350	1·25	73·7	63·80	4·70	92·9	2	15
11.	50	350	1·25	73·7	67·31	2·65	94·9	5	0
				B.					
12.	50	200	1·25	73·7	66·26	1·82	92·9	2	20
13.	50	200	1·25	73·7	65·30	5·27	95·8	3	0
14.	50	350	1·25	73·7	66·05	2·90	93·6	3	45
15.	50	350	1·25	73·7	68·75	1·57	95·4	4	30
16.	50	200	10	73·7	59·10	5·43	87·4	0	20
17.	50	200	10	73·7	67·90	1·50	94·2	2	25
18.	50	200	10 (*a*)	73·7	68·32	3·30	95·8	1	45
				C.					
19.	50	200	1·25	73·7	67·60	1·80	94·2	2	10
		150	10					1	0
20.	100	300	1·25	147·4	132·80	6·32	94·4	2	0
		200	10					1	15
21.	50	200	1·25	73·7	69·50	2·50	97·7	1	25
		100	10					1	0
22.	100	300	1·25	147·4	135·25	4·81	97·5	2	0
		200	1·25					1	0

(*a*) And gaseous.

bath at 60° under a pressure of 15 mm., that the weight of the ester was diminished by less than 0·05 grm.

From these experiments it appears that the losses in the preparation of pure succinic ester should not exceed 2 grms.

While the general process of treatment described above was applied in all the experiments recorded in the table, some experiments differed from others in respect to the proportions of the reagents and to supplementary treatment.

In the experiments of Series A of the table the alcohol used was 99·5 per cent pure, and this was charged with dry gaseous hydrochloric acid to the amount of 10 grms. to the litre. The succinic acid was the pure acid of commerce.

In the experiments of Series B, the alcohol used was made more nearly absolute than that used in Series A by heating 99·5 per cent alcohol for an hour over fresh calcium oxide with a return condenser, and distilling to a protected receiver open to the air through a calcium oxide tube. In Experiments 12, 13, 14, and 15 succinic acid prepared pure by hydrolysis of the ester in the presence of nitric acid was used, in the others the acid of commerce. The alcohol was charged with dry hydrochloric acid to the amount of 10 grms. to the litre. In 16 and 17 the alcohol was charged with dry hydrochloric acid to the amount of 80 grms. to the litre, and in Experiment 18 the alcohol originally charged with 80 grms. to the litre was reinforced by passing into the sideneck flask a rapid current of hydrochloric acid gas, dried by passing through concentrated sulphuric acid in a bead tower of 30 centimetres length, simultaneously with the charged alcohol vapour.

An inspection of the yields obtained in the experiments of Series B, in which the more nearly absolute alcohol was employed with experiments otherwise nearly similar of Series A in which alcohol of 99·5 per cent purity was used, show perhaps a trifling advantage in favour of the slightly stronger alcohol. Thus, 12 of B gave 1 per cent more yield than 6 of A, though in the latter 25 per cent more of the charged alcohol was used under conditions otherwise closely similar; 13 of B gave about the same yield as 7 of A, though in the latter 25 per cent more of the charged alcohol was used; but the yield in 15 of B with an increase of 16·6 per cent in the amount of charged alcohol and 12·5 per cent in the reaction time was a trifle less than that of 8 of Series A.

Upon examining the yields of experiments in which equal amounts of the alcohol similarly charged were brought into action with a given amount of succinic acid, it appears, as is natural, that the amount of succinic ester produced increased with the time of reaction. This inference becomes evident in a comparison of Experiments 1 and 2, 6 and 7, 8 and 9, 10 and 11, 12 and 13, and 14 and 15.

It appears also that the proportion of similarly charged alcohol, for a given weight of succinic acid, affects the yield of ester—very markedly at first, but that the effect of increasing beyond a moderate limit the amount of alcohol passed through the apparatus in a given time is not so important. This effect is not surprising when it is remembered that the larger part of the water liberated is found early in the reaction, and that the effect of the continued distillation would be naturally more in evidence at that time. Thus the yield of Experiment 3, in which 150 cc. of the charged alcohol were used, is 8 per cent greater in half the reaction time than that of Experiment 1, in which 100 cc. of the same mixture were employed; while the difference between the yield of 6 from 250 cc. of the charged alcohol and that of 10 from 350 cc. of the similarly charged alcohol is 1·1 per cent. In 12 of B with purer acid and alcohol of greater concentration the process gives the same yield as in 10.

Increase in the amount of dry hydrochloric acid with which the alcohol is charged is effective in increasing the yield. From 18 it appears that a current of dry hydrochloric acid has such an effect. This appears when 18 is compared with 17, and more strikingly when compared

with 5, where the differences are largely the concentration of the hydrochloric acid with a gain of 4 per cent in the yield of 18.

In the experiments of Series C the process of forming the ester was conducted in two stages in an attempt to cause the esterification of the final portions of the succinic acid more advantageously. It is obvious from the work recorded in Series A and Series B that it is comparatively easy to cause the esterification of a little more than 90 per cent of the acid. In Experiment 19, after the first portion of alcohol—200 cc.—of highest purity charged with dry gaseous hydrochloric acid in the proportion of 10 grms. to the litre had acted upon the commercial succinic acid in the manner described above, a fresh portion of alcohol, 150 cc., containing 10 per cent of dry hydrochloric acid gas was put with the ester solution, and the whole was heated at the boiling-point for an hour with a return condenser in an attempt to learn whether a fresh mass of the absolute alcohol hydrochloric acid mixture containing 10 per cent of hydrochloric acid could serve sufficiently as a dehydrating agent to allow the completion of the reaction. It does not seem evident that the second treatment is markedly advantageous in completing the reaction. Its effect, if anything, is slight. In case of Experiment 20, after completing esterification of the pure acid so far as possible with 200 cc. of the purest alcohol with hydrochloric acid in the usual way, 200 cc. more of the same alcohol with 10 per cent of hydrochloric acid was driven through the ester as in the first half of the procedure. The effect of this second treatment is not apparently of marked advantage in esterifying the final portions of the acid. In Experiments 21 and 22 after the treatment for esterification, as given earlier, was completed, all low boiling-point material, chiefly alcohol, water, and hydrochloric acid, was removed from the ester in the sideneck flask by a vacuum fractionation, carried out by heating the flask in a water-bath finally at 60° with the pressure on the manometer registering 15 mm., this pressure and temperature being maintained fifteen minutes. The material in the flask was then treated with fresh alcohol and hydrochloric acid in amounts given in the table in gaseous form as in the first half of the experiment. Pure succinic acid was used in case of 21, and commercial acid in case of 22. This process of removing traces of water by the intermediate vacuum distillation from the mixture containing the ester is obviously very effective, and the yield of Experiment 21 is the best of the entire suite. Indeed, if it be recalled that the losses inherent in the processes of obtaining the pure ester are a fraction more than a grm., it is seen that all of the acid taken appears as ester except a portion as small as 0·30 of a grm.

So it appears that while high purity of the succinic acid and the alcohol, the proportion of the hydrochloric acid, the time of the reaction, are all influential factors in the process of forming the ethyl ester, the thing most important in obtaining a high yield is the removal of the water as it is formed in the reaction; and we have found that this may be done most easily and very effectively by passing the vapour of alcohol charged with a small proportion of hydrochloric acid into a continuously distilling mixture of succinic acid and alcohol also charged with hydrochloric acid. By thus acting with a total volume of 300 cc. of the alcohol charged with 1·25 per cent of hydrochloric acid upon 50 grms. of succinic acid, the yield in action of five hours reached 97 per cent of the theory, while this time of action was cut in two, and the yield at the same time slightly increased to 97·7 per cent by interpolating in the process a vacuum distillation to remove water more effectively from the reacting mixture.

Even if the usually small amounts of ester which pass to the distillate are disregarded in the process of recovery, the yield of the process in its simpler form is still 20 per cent higher than that of any other described procedure known to us for making the ethyl ester of succinic acid by the interaction of the acid and alcohol.—*American Journal of Science*, xxiii., p. 368.

NOTICES OF BOOKS.

The Medico-Physical Works of John Mayow, LL.D., M.D. Edinburgh: The Alembic Club; James Thin. London: Simpkin and Co. 1907.

The Alembic Club has already won the gratitude of students of historical chemistry, who find their reprints of the classics of the science of great value and interest, and this seventeenth volume of the series will be particularly welcome, for it contains the works of Mayow, which have hitherto been almost inaccessible to English readers. The translation has been performed literally from the edition of 1674, printed at Oxford, and in order that the reader's survey of Mayow's views may be as far-reaching and correct in detail as possible the whole of his scientific works are included. The five treatises show that he was far in advance of his time as regards his ideas about chemical phenomena, more especially on the nature of combustion, and he showed considerable skill in devising and adapting experimental methods, the quaint illustrations of his apparatus which are reproduced revealing his great ingenuity. The papers are not provided with explanatory notes or comments, which indeed they do not require, for Mayow's language was very clear, and it is easy to grasp his meaning and follow his argument, even when he uses unfamiliar phrases or words to describe the phenomena he observed. His physiological work was almost on a level as regards importance with his chemical discoveries, and the advances due to him in the two branches together give him a strong claim to be regarded as one of the most eminent of English men of science.

The Physiology of Alimentation. By Dr. Martin H. Fischer. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

This book gives an account of the physiology of alimentation, more especially from a medical point of view. It opens with a lengthy discussion of the mechanical phenomena of alimentation, which is excellently illustrated by reproductions of X-ray photographs, sent to the author by Dr. Cannon. Then the chemical constituents of the juices which act upon the food are considered, and much attention is paid to the subject of ferments and fermentation. This part of the book appears to be well up to date, and some specially interesting or important subjects, as, for example, Weinland's work upon antiproteinase, are discussed fully; the bacteriology of the alimentary tract is also well treated. The later part of the book deals with the alimentary tract as an absorptive and as an excretory system, and here the author appears to have committed an error of judgment in assuming that his readers would require an exposition of the elementary laws of osmosis. However, the whole book, while not aspiring to be an important original contribution to physiological literature, or even a complete text-book on the subject of alimentation, bears evidences of careful, well-planned work, and the subject is handled in a particularly interesting manner.

Water Analysis. By J. Alfred Wanklyn, M.R.C.S. Eleventh Edition, revised by W. J. Cooper. London: Kegan Paul, Trench, Trubner, and Co., Ltd. 1907.

The late Professor Wanklyn's experience of the analysis of water was extensive, and his text-book on the subject has long been regarded as an important authority. The eleventh edition is a reprint of the tenth, giving detailed descriptions of methods of carrying out analyses, both for general sanitary and special purposes, together with useful notes on the usual methods of drawing up reports and the conclusions to be drawn from the results of experimental work. The book contains in addition a short biographical memoir of Prof. Wanklyn, in which an account is given of his work upon various chemical subjects, some of which was of considerable importance.

The Evolution of Matter, Life, and Mind. By W. Stewart Duncan. Philadelphia: Index Publishing Company. 1907.

The Preface to this book arouses in the reader hopes which a very short examination of the text shows are not destined to be realised. An exposition of monistic philosophy as applied to psychical science should be interesting, and a well-balanced criticism of the theory of psycho-physical phenomena would be welcomed by the many who feel that the time is ripe for a great advance of our knowledge of this subject. But the book falls far short of the standard which a guide to modern thought should reach, and the writer does not exhibit that tolerance and moderation without which any book upon a polemical subject is almost worthless. He wastes much space in proving what the majority of his readers will regard as already firmly established, and lays undue stress upon such of his own prophecies as appear to be justified by facts, while at the same time losing no opportunity of criticising those who do not agree with him or who paid scant attention to his theories. The reader will therefore be not unprepared to find that some of the most sweeping statements are at any rate open to question in the form in which they are put forward, and when he reads that to call a chemical compound by its name, even if it possibly appears unwieldy to the uninitiated, is mere bluffing and fooling, as if chemical names, such as paraoxyphenetol, were a purely empirical means of identifying substances, used as blinds to conceal their real nature, he will not be surprised at anything that comes later. The author has evidently still to learn what the term "organic" means when applied to a chemical compound.

Organic Chemistry for Advanced Students. By Julius B. Cohen, Ph.D., B.Sc. London: Edward Arnold. 1907. Pp. 632.

In his Preface the author informs us that this book is not in any way to be looked upon as a book of reference. It has been prepared from notes of a series of lectures delivered to advanced students, and therefore assumes that the reader is already well acquainted with the principles of organic chemistry.

It would be impossible, even in a book of this size, to deal adequately with all the various developments of so large a subject; and as the tendency now-a-days is to specialise in every subject, so, in this volume, has the author specialised on a certain number of sub-divisions of organic chemistry.

The book is divided into fourteen chapters, beginning with an historical introduction. In Chapter II. he deals with isomerism and stereoisomerism, followed by chapters on the stereochemistry of unsaturated and cyclic compounds and the stereochemistry of nitrogen. Chapters V., VI., and VII. are devoted respectively to isomeric change, steric hindrance, and condensation. Up to this point the author has dealt principally with theories, typical reactions, and changes, but in Chapter VIII. we come to the carbohydrates, which are among the principal products of plant life, and include the important group of the saccharoses.

Fermentation and enzyme action are the subjects of Chapter IX., followed by the purine group, which comprises uric acid and the xanthine bases, in the succeeding chapter.

Chapter XI., on the proteins, embraces a large and ill-defined group of substances derived directly or indirectly from living matter; they form the chief constituents of the protoplasm of the majority of cells and enter into the composition of animal tissues and secretions; they are classified on pages 412—415.

The benzene theory next engages our attention, commencing with Kekulé's benzene formula, followed—some pages further on—by Kekulé's dynamic hypothesis and the dynamic formula for benzene.

Chapter XIII. is on the terpenes and camphors—an important group, comprising natural and artificial perfumes.

The alkaloids form the subject of Chapter XIV. and last. These consist of numerous oily and crystalline basic substances obtained from certain plants, and are characterised by very marked physiological properties, making them of special interest both to the chemist and physiologist. The history of the successive stages in the synthesis of these bodies is the main object of this chapter.

The book is one of considerable interest, and though not compiled on the lines of an orthodox text-book, we feel sure that it will be well received by those who are going beyond the ordinary college course of organic chemistry. It is well printed in large clear type and provided with two excellent indices, one of "subjects" the other of "authors."

CORRESPONDENCE.

RELATION BETWEEN THE ATOMIC WEIGHTS OF THE ELEMENTS.

To the Editor of the Chemical News.

Sir,—If we consider a table showing Mendeleeff's classification of the elements, it will be found that the members of each group are very nearly made up of ascending multiples of the top member of each group added to a regular multiple of the number 16. To illustrate, I give Group I. of Mendeleeff's classification:—

New series.			Difference.
0.		Li = 7·03	
1.	16 + 7·03 = 23·03	Na = 23·05	0·02
2.	2 (16) + 7·03 = 39·03	K = 39·1	0·07
3.	3 (16) + 2 (7·03) = 62·06	Cu = 63·6	1·54
4.	4 (16) + 3 (7·03) = 85·09	Rb = 85·4	0·31
5.	5 (16) + 4 (7·03) = 108·12	Ag = 107·9	0·22
6.	6 (16) + 5 (7·03) = 131·15	Cs = 132·9	1·75
7.	7 6	—	
8.	8 7	—	
9.	9 (16) + 8 (7·03) = 200·24	Au = 197·2	3·04

We may express the above relation in an empirical formula, thus—

$$mx + (m \pm n)y = W;$$

where m = number of series (He series = 0), x = 16, y = the top member of the group, and n = a positive or negative integer between 0 and 5.

A table can be arranged so that n has a regular + value in the F, Fe, Co, Ni groups and a − value in all the others. To illustrate this, and also the effect of giving y a slightly different value in some cases, I give the Be group:—

Series.			Difference.
0.	y = 8	Be = 9·1	1·1
1.	16 + 8 = 24	Mg = 24·1	0·1
2.	2 (16) + 8 = 40	Ca = 40·1	0·1
3.	3 (16) + 2 (8) = 64	Zn = 65·4	1·4
4.	4 (16) + 3 (8) = 88	Sr = 87·6	0·4
5.	5 (16) + 4 (8) = 112	Cd = 112·4	0·4
6.	6 (16) + 5 (8) = 136	Ba = 137·4	1·4
7.	7 6		
8.	8 *6	*n = 2	
9.	9 (16) + 7 (8) = 200	Hg = 200	0
10.	10 (16) + 8 (8) = 224	Rd = 224	0

Except in the Li group, n changes in value at the 4th or the 8th series in each group.

Might not this relation be used to explain Sir William Ramsay's recent discoveries concerning the disruption of different elemental atoms by the Rd emanation? Accepting for the moment the supposition that the atoms are made up of groups, as indicated above, and that group 16 is a

strong base or radicle, and also that the atomic weight of the α-particle is 2, then upon bubbling the emanation through water we might get the following reaction:—

$$H_2O^* + 2\ \alpha\text{-particles} = (16+4) + H_2$$
$$= \dagger Ne + H_2$$

* O=16. † Ne=(16+4)=20.

Or taking another case (see Li group above)—

$\{3\ (16) + 2\ (7)\} + 2\ \alpha$-particles $= \{2\ (16) + 4\} + (16+7) + 7$;

in other words,—

$$Cu + 2\ \alpha\text{-particles} = Ar + Na + Li.$$

I would very much like to know whether these relations have ever been pointed out before, and, if so, where I can find an account and explanation of it.—I am, &c.,

W. DENHAM VERSCHOYLE.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 12, September 16, 1907.

Method of Rapidly Determining Carbon and Hydrogen in Organic Substances.—Pierre Breteau and Henri Leroux.—The combustion tube consists of an outer nickel tube into which an inner porcelain or quartz tube is fixed. The latter has rolled round it a platinum spiral, which can be raised to a dull red heat by means of an electric current. The substance to be burnt is placed in a porcelain boat, and is introduced into the combustion tube in a glass tube to which a semi-capillary tube is fused. The glass tube is placed so that one or two turns of the platinum spiral are within the wide part. A current of dry oxygen enters the glass tube by the semi-capillary, and another circulates round the outside of the glass tube. The further end of the nickel tube is connected with the absorption apparatus. When the platinum spiral is dull red the substance is very gently heated. The combustion is proceeding satisfactorily when a small flame is seen playing round the end of the spiral. When the substance has been decomposed the residual carbon is heated strongly, the rate of the inner current of oxygen being greatly increased. A combustion takes from fifteen to forty minutes, according to the nature of the organic substance.

No. 13, September 23, 1907.

Methylation of Ethyl Alcohol from the Point of View of the Tendency of the Haloid Ethers to Isomerise.—Louis Henry.—It is a remarkable fact that the alcohols and their acetic ethers are structurally stable, while the haloid ethers readily isomerise. This isomerisation leads to the fixation of the halogen atom in a carbon chain containing less hydrogen, and even in the least hydrogenated chain. Sometimes the carbon nucleus itself remains intact, and sometimes it undergoes a deep-seated change in its structure, thus:—

$CH_3—CH_2—CH_2X$ isomerises to $CH_3—CHX—CH_3$

$H_3C>CH—CH_2X$ „ „ $CH_3>CX—CH_3$

$H_3C\diagdown H_3C>C—CH_2X$ „ „ $H_3C>CX—CH_2—CH_3$.

These isomeric transpositions are effected with different degrees of facility. When the different groups of haloid ethers corresponding to the alcohols $C_nH_{2n+1}OH$, which can be attached by methylation (*i.e.*, replacement of hydrogen fixed to carbon by $—CH_3$) to the simplest of the polycarbon alcohols (ethyl alcohol, C_2H_5OH), are considered, the general conclusion drawn is that the isomerisation of the haloid ethers is effected most easily when there is least hydrogen in the neighbourhood of the ether haloid chain or in the chain itself. The trimethyl haloid ethers, $(CH_3)_3\equiv C—$, are particularly remarkable in this respect. This is another instance of the stability which the presence of much hydrogen gives to polycarbon nuclei.

Various Cast Irons.—Léon Guillet.—The author has already shown that silicon and aluminium favour the formation of graphite, while the presence of chromium tends to prevent it. Nickel resembles silicon and aluminium in this respect, and thus the general conclusion to be drawn from these researches is that elements which can dissolve in iron lead to the formation of graphite, while elements which form a double carbide with cementite (manganese and chromium) hinder it.

MEETINGS FOR THE WEEK.

THURSDAY, 24th.—Chemical, 8.30. "Constitution of Phenol- and Quinol-phthalein Salts—a Contribution to the Quinonoid Theory of Colour," by A. G. Green and P. E. King. "Poly-ketides," by J. N. Collie. "Production of Orcinol Compounds by the Action of Heat on the Sodium Salt of Ethylacetoacetate," by J. N. Collie and E. R. Chrystall. "Simple Gas Generator for Analytical Operations, by J. M. Sanders. "Some Double Ferrocyanides of Calcium, Potassium, and Ammonium," by J. Campbell Brown. "Halogen Determination in Organic Substances," by J. Moir. "Racemisation by Alkali as applied to the Resolution of γ-Mandelic Acid into its Optically Active Isomerides," by A. McKenzie and H. A. Müller. "Optical Activity of Cyclic Ammonium Compounds," by F. Buckney and H. O. Jones. "Keten, a New Anhydride of Acetic Acid," by N. T. M. Wilsmore. "Action of Phosphorus Pentachloride on Hydroxytrimethyl-succinic Ester, 1.2.2-Dimethyltrimethylene-1.2-dicarboxylic Acid," by H. Henstock and B. E. Woolley.

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By GEOFFREY MARTIN, B.Sc., Ph.D.,

Lecturer and Demonstrator in Chemistry at Univ. Coll., Nottingham.

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2500.

THE FRUIT OF THE *CELESTRUS SCANDENS* AND *SOLANUM DULCARUM*.

By A. A. WELLS and GRANT S. REEDER.

The fruit of the *Celestrus scandens*, climbing bitter-sweet, was gathered in some low waste places near Mount Vernon in Eastern Iowa in the autumn of 1904. It was kept at the air temperature until January, 1907, when work upon it was begun.

The berry thus dried when separated from the pod weighed about 0·152 grm. After igniting thoroughly in a platinum crucible the ash was found to weigh 0·005 grm.

The seeds can easily be separated from the pulp by gently squeezing the berry in the hand. Each berry contains from four to six seeds, which are similar in size and colour to raisin seeds. The berries contain such a large amount of sugar that in the air they do not lose more moisture nor become drier and harder than the raisin as it is ordinarily found. The pulp surrounds the seeds in a relatively thin layer, representing not more than one-quarter of the entire bulk of the berry.

The pod which encloses the berry is composed of three sections; these open as the fruit ripens. The inside of the pod is of a light orange colour, the outside of a much darker shade. The fruit grows in clusters, somewhat suggesting clusters of grapes.

There were on hand for the analysis about six and a-half quarts of berries, with the pods. The berries were separated from the pods by hand, which proved to be a slow process, and there were found to be three pints. These were transferred to a flask, covered with distilled water, and kept at nearly the boiling temperature for forty-eight hours. The liquid was then drained off, and the berries set aside for further work upon them.

The water extract gave a satisfactory test for sugar with Fehling's solution, and to determine the kind a portion of the liquid was evaporated nearly to dryness on the water-bath. As the drying continued no amount of stirring would give a crystalline mass, although it became hard enough to break into chunks. Upon standing in the air for some time the mass was deliquescent and appeared like a thick syrup.

The sugar was treated with phenylhydrazine in varying proportions, but the most satisfactory results were obtained by taking 0·1 grm. sugar, 0·2 grm. phenylhydrazine hydrochloride, and 0·3 grm. sodium acetate. The mixture was placed in a test-tube with 10 cc. distilled water. This was loosely corked and kept in a bath of boiling water. After two minutes a precipitate resulted, indicating that the sugar is fructose. The experiment was repeated several times, the results pointing in the same direction.

The remaining portion of the water extract was further tested; the solution gave a distinct acid reaction with litmus, showing the presence of a free acid or an acid salt. Upon the addition of calcium chloride to an alkaline solution, a precipitate soluble in acetic acid resulted, indicating the presence of a tartrate. Ferric chloride was added to another portion, and the resulting black colour indicated either tannic or gallic acid. Upon the addition of a little potassium cyanide a red colour was obtained, showing that it is gallic acid. Lead acetate was next added, when an orange-coloured precipitate, soluble in acetic acid, resulted. This is a test for the colouring matter fisetin. To verify this, we added a solution of stannous chloride and obtained the characteristic orange precipitate.

The ash of the berries effervesces in hydrochloric acid. The carbonate doubtless results from the decomposition of an oxalate.

The seeds were separated from the pulp by placing the berries in water and rubbing them between the hands. The loosened pulp was removed by running water, in the manner of "panning" ore. The seeds were dried and treated in a flask, to which was attached a perpendicular condenser, with successive portions of boiling alcohol, for forty-eight hours.

The alcoholic solution was poured off, and upon the addition of water it became turbid and had the odour and colour of sweetened chocolate in milk. This was distilled with steam and the distillation continued for a number of hours. The distillate had a pleasant nut-like odour, which disappeared on exposure to the air; no trace of oil other than this odour was observable in the distillate. During the process of distillation a resinous substance collected around the flask and appeared as a scum on the liquid. On cooling the contents of the flask nearly to zero, the substance became solid and was easily separated. By treating this with warm alcohol a portion dissolved, and, upon filtering, the insoluble residue was found to be a dry, tasteless, and odourless substance of a chocolate appearance. On adding water to a small portion of the filtrate in a test-tube, the turbidity reappeared as before the distillation with steam.

The alcohol was removed by distillation, and a yellow oil remained, with an odour similar to that which went over in the distillation with steam. An alcoholic solution was treated with bone-black and further purified by treating alternately with alcohol and ether. It crystallised in needles which melted at 62°; it is therefore palmitic acid.

After drying the seeds that had been treated with alcohol, they were crushed in a mortar, placed in a flask connected with an inverted condenser, and treated for several hours on a warm water-bath with successive portions of ether. Two oils were extracted by this process, one of which is soluble and the other insoluble in alcohol. The two oils could be separated by treating several times with alcohol in a separating funnel, the alcoholic solution rising to the top. The soluble oil was lemon-yellow in colour, the insoluble one was orange. We were unable to crystallise either oil.

The soluble oil was first saponified by treating it with an alcoholic solution of caustic potash. Afterwards, by treating it a number of times with ether, a solid was obtained which melted at 16°; this indicated olein with a slight admixture of palmitin. The other oil, when saponified and purified with ether in the same way, gave a solid with a higher melting-point, but not sufficiently high for palmitin. As a small quantity of palmitic acid was obtained from the alcoholic extraction, it seemed reasonable to infer that this oil also was a mixture of olein and palmitin, in which the palmitin predominated.

The pods were treated in the same manner as the pulp of the berries, and were found to contain the same substances.

The Solanum dulcamara.

The *Solanum dulcamara* (deadly nightshade) berries were gathered August 20, 1906, at Sylvan Beach, New York, where they grow in rich profusion. They greatly add to the charm of the river banks of that wild and interesting region. Thoreau writes regarding them:—"The berries are another kind which grow in drooping clusters. I do not know any clusters more graceful and beautiful than these drooping cymes of scented or translucent cherry-coloured elliptical berries. They hang more gracefully over the river's brim than any pendant in a lady's ear. Yet they are considered poisonous, not to look at, surely. But why should they not be poisonous? Would it not be bad taste to eat these berries, which are ready to feed another sense?"

About 100 grms. of the berries, which had been thoroughly dried and pulverised in a meat grinder, were placed in a 500 cc. flask fitted with a perpendicular con-

denser. These were treated with ten successive portions of hot alcohol, making use of the water-bath. The alcoholic extract was deeply coloured red. The alcohol was removed by distillation, and there remained a thick sticky substance, brown in colour, with an odour similar to molasses. The substance was easily shown to contain sugar by its reduction of Fehling's solution. The treatment with alcohol did not remove all the colour from the fruit. Several portions of hot water were afterwards added, which extracted all the red colour. The water extract was found to contain sugar.

A portion of the liquid extract was heated in a beaker glass, and ammonia and calcium chloride were added. A small precipitate soon appeared. This was filtered cold to allow the citrate, if any were present, to pass through. The precipitate dissolved in acetic acid, indicating tartaric acid. The tartaric test was confirmed by diluting a portion of the liquid extract largely with water, adding 2 cc. of acetic acid, a few drops of a solution of potassium acetate, 15 grms. of finely powdered potassium chloride, and 20 cc. of alcohol. After standing about twenty hours quite a heavy precipitate appeared.

Two grms. of the berries were placed in a platinum crucible. These were gently heated at first, and the heat was gradually increased. There was noticed an odour of burnt sugar, which became stronger with increase in temperature, but at no time disagreeable. On the addition of hydrochloric acid to the residue there was a brisk effervescence. The acid filtrate showed a slight trace of calcium.

A portion of the liquid extract was rendered alkaline with caustic potash solution, lime-water was added, and a precipitate formed on boiling. This was filtered off, re-dissolved, and re-precipitated with caustic potash and lime-water, confirming the test for citric acid.

The reaction for potassium was easily shown by wrapping a piece of platinum wire around a berry and holding it in a Bunsen flame.

The Tests for Atropine.—A small portion of the liquid extract was taken, and a solution of tannic acid added. The large brownish precipitate showed the presence of atropine. The precipitate was dissolved in hydrochloric acid and tannic acid was again added, when the brown precipitate again appeared. To another small portion of the liquid extract a solution of iodine in potassium iodide gave a precipitate of atropine. A solution of ammonium metavanadate in sulphuric acid gave a red precipitate, also a test for atropine. The fruit has long been noted for its large atropine content.

The sugar was examined by the time required for osazone formation with phenylhydrazine hydrochloride in the presence of sodium acetate. Two-tenths of a grm. of the dried sugar, three-tenths grm. sodium acetate, and 2 cc. of water were placed in a test-tube, which was immersed in a hot-water bath. The time of the osazone formation was noted. About fifty tests were made, and the time was between one and two minutes, indicating fructose. The osazone was purified by repeated crystallisation, and under the microscope showed the needle-like crystals which melted at 170°.

The Oils.—The nutlets contained in the 100 grms. of fruit were ground to a fine powder, placed in a Soxhlet apparatus, and treated with hot ether for seventy-two hours. About 10 cc. of oil was extracted. This was placed in a small open flask, and a portion seemed to evaporate after standing a few hours; that which remained possessed an odour resembling nut oil. About 400 grms. of the nutlets were next taken and extracted with ether as before; this gave sufficient oil for the tests. It was saponified with a solution of caustic potash. One portion of the oil remained liquid, while a second portion (after purification) became a solid. The melting-point of this indicated a mixture of palmitin and olein.

We desire to express our thanks to Professor N. Knight for suggestions and help in this work.

Chemical Laboratory, Cornell College,
October 2, 1907.

THE CATHODIC PRECIPITATION OF CARBON.

By WILLIAM BLUM and EDGAR F. SMITH.

Some years ago one of us called attention to the electrolytic precipitation of iron, by the current, from citrate and tartrate solutions (Smith, *Am. Chem. Journ.*, x., 330; and *Journ. Analytical and Applied Chemistry*, v., 488). In doing so, mention was made that on dissolving the deposited metal "in dilute cold sulphuric acid a strong odour of hydrocarbons was perceptible." Later, reference was again made to this fact and conditions given, observing which, the contamination of the metal by carbon might be avoided (Smith's "Electro-chemical Analysis," 3rd Ed., p. 100). In electro analysis, the question of the contamination of metals by carbon, if the metals have been precipitated from organic electrolytes, has been quite freely discussed. However, the contamination in nearly all instances has been regarded as a result of carelessness in manipulation, and may be avoided.

During the past summer we made observations, on the conduct of certain organic acids under the influence of the current, which seem of value; hence a brief account of them is submitted in this communication.

To begin, it was tried to ascertain the degree of reduction of oxalic acid at the cathode. The gasometric method was called into use, *e.g.*, a comparison of the volume of hydrogen evolved in the cell with that liberated in a voltameter in the same period. It soon became evident that this procedure would not be delicate enough to detect any such reduction. However, while occupied in this way with an ammoniacal tartrate solution, a black deposit made its appearance on the cathode. When held in the flame it burned off completely from the platinum plate. The latter had an area of 100 sq. cm. Several actual trials may be here introduced. Thirty-seven and one-half grms. of tartaric acid were dissolved in water, neutralised one-half with ammonia, then diluted to a litre. Portions of this solution were electrolysed at a temperature of 60° C. The anode was a platinum spiral suspended in a porous cup. The cathode was the foil to which reference has been made. A current of 1 ampère and 12½ volts acted for a period of two hours. A black deposit showed itself on the cathode. It burned off in the flame. In another experiment, with conditions like those just mentioned, discarding, however, the cup, there was no deposit on the cathode, but the solution was deep yellow in colour. Again, in electrolysing a portion of the ammonium tartrate without the porous cup, but surrounding the anode with a muslin bag, at the ordinary temperature, with a current of 4 ampères and 6 volts, there was a very considerable deposit, black in colour, on the cathode. It burned away, with the exception of a mere iridescence, when held in a flame. In another experiment, 15 grms. of tartaric acid were neutralised with ammonia, diluted to 150 cc., and electrolysed at 60° C., for four hours, with a current of 4 ampères and 6 volts. The anode and cathode had both been weighed. The cathode became coated with a greyish black deposit. The anode sustained a loss in weight, and only one-third of the cathodic deposit was carbon, the remainder being platinum, which had come from the anode.

Upon substituting a solution of citric acid (70 grms. to the litre) and electrolysing at 70° C., for three hours, with a current of 1 ampère and 16 volts, a heavy black deposit separated on the cathode. It was not affected by hydrochloric acid. It burned away completely in a Bunsen flame. The electrodes were separated by a porous cup. In other experiments a muslin bag surrounded the anode. This bag had previously been well soaked in caustic soda. The usual black cathodic deposit was obtained. It burned away completely on heating. On digesting this deposit with chromic acid, carbon dioxide was obtained and recognised by its reaction with lime water.

Another trial is worthy of notice. In it a half normal solution of ammonium citrate, made alkaline with ammonia,

was electrolysed for a period of five hours with a current of 4 ampères and 6 volts. The anode was protected by a muslin bag. The solution rapidly took on a yellow colour, a distinct odour of acetamide was evolved, and a black deposit appeared upon the cathode. It both burned on heating and generated carbon dioxide with a chromic acid mixture. It may be added that the solution was not heated from without as it developed a great deal of heat during the passage of the current.

Similar results were obtained on electrolysing a like solution without a diaphragm.

Other experiments were as follows:—

1. Five grms. of sodium citrate and 1 grm. of citric acid were dissolved in 150 cc. of water and electrolysed at 60° C., for five hours, with a current of 4 ampères and 11 volts. There was a brass-like deposit on the cathode. It weighed 0·0018 grm., while the anode had lost 0·0014 grm.

2. Fifteen grms. of citric acid, neutralised with ammonia and diluted to 150 cc., were electrolysed at 60° C., for four hours, with a current of 4 ampères and 6 volts. A greyish black deposit separated on the cathode. It equalled 0·0014 grm., which represents carbon. The anode lost in all 0·0103 grm. in weight.

In the many trials made, the solutions gradually acquired first a pale yellow colour, which in turn passed to brown and at times almost black without becoming turbid. However, it must be said that solutions of ammonium oxalate, ammonium formate, ammonium acetate, and ammonium succinate did not yield black deposits to the cathode. In solutions of ammonium lactate and benzoate they appeared as readily as in tartrate and citrate solutions.

This deposition of carbon upon the cathode is extremely interesting. In 1896, Coehn (*Zeit. Elektrochemie*, 1896, p. 541) called attention to the fact that when carbon was made an anode in the electrolysis of sulphuric acid, the latter became at first yellow, and by prolonging the experiment, dark red and reddish brown in colour. If this meant a solution of carbon the latter must presumably be in the form of ions, *e.g.*, in a form directable by the current. It must be in a form which, as it does not decompose water, would appear at the anode. With these thoughts before him, Coehn electrolysed sulphuric acid of varying concentration with an anode of carbon and a cathode of platinum. The result was a splendid deposition of carbon on the cathode. It burned away completely on heating, and gave carbon dioxide when acted upon with a chromic acid mixture. In later experiments, Coehn was able to determine in the electrolytic way the equivalent of carbon, and found it to be 3.

Turning to our observations with tartaric and citric acid, it must be that these are broken down at the anode during electrolysis; that the carbon thus liberated from combination in these acids enters aqueous solution as a hydrate of which the carbon is cation, and this, under influence of the current, passes in its ionic form to the cathode just as a metal in some salt does under similar influence. When, therefore, iron is deposited from a citrate or tartrate electrolyte, the carbon ions wander with the iron ions to the cathode, and there an alloy of iron and carbon appears. This alloy, on treatment with dilute sulphuric acid, generates hydrocarbons. Very little, if any, of the carbon deposited with iron is graphitic. It is chemically combined. Just as zinc and copper from certain electrolytes separate as brass, so do the carbon and iron separate as an alloy from the electrolytes which have been under discussion.

The conclusions warranted from the experiments here noticed, and many others like them, are:—

1. Carbon is deposited on the cathode from solutions containing tartaric, citric, lactic, and benzoic acids. This is particularly the case if a stationary anode be used along with high current density.

2. From solutions like those in 1, where high current density is employed, platinum will dissolve from the anode and be precipitated in part upon the cathode.—*Proceedings of the American Philosophical Society*, xlvi., p. 59.

THE MOLECULAR WEIGHT OF ARGENTIC SULPHATE, AND THE ATOMIC WEIGHT OF SULPHUR.*

By THEODORE WM RICHARDS and GRINNELL JONES.

Introduction

The atomic weight of sulphur has been investigated by many experimenters, but, as will be seen, the results are far from concordant. A brief review of these investigations forms the most appropriate introduction to the present one. The values in the following list have been re-calculated with modern figures for the other atomic weights involved (Ag = 107·93, Cl = 35·473, Pb = 206·9, Hg = 200·0, Na = 23·008, C = 12·002):—

1814	Berzelius (*Phil. Trans.*, civ., 20)	32·0
1826	Berzelius (*Pogg. Ann.*, viii., 15)	32·08
1833	Turner (*Phil. Trans.*, cxxiii., 539)	32·00
	Ditto	32·06
1836	Thomson (*Journ. Prakt. Chem.*, viii., 370)	32·
1844	Erdmann and Marchand (*Journ. Prakt. Chem.*, xxxi., 396)	31·99
1845	Berzelius ("Lehrbuch," 5th Ed., iii., 1187)	32·04
	Ditto	32·16
1848	Svanberg and Struve (*Journ. Prakt. Chem.*, xliv., 320	32·15
1851	Struve (*Liebig's Ann.*, lxxx., 203	31·94
1859	Dumas (*Ann. Chim. Phys.*, [3], lv., 148)	32·00
1860	Stas (*Bull. Acad. Belg.*, [2], x., 153, 322)	32·06 (*a*)
1878	Cooke (*Proc. Amer. Acad.*, xiii., 50).. ..	32·137
	Ditto	31·980
1891	Richards (*Proc. Amer. Acad.*, xxvi., 268)	32·043
1898	Leduc (*Ann. Chim. Phys.*, [7], xv., 94)	32·056
1899	D. Berthelot (*Journ. de Phys.*, [3], viii., 271)	32·050
1904	Jaquerod and Pintza (*Comptes Rendus*, cxxxix., 129)	32·01
1905	Guye (*Comptes Rendus*, cxl., 1242)	32·065
1905	Jaquerod and Scheuer (*Comptes Rendus*, cxl., 1384)	32·036

(*a*) Van der Plaats (*Ann. Chim. Phys.*, 1886, [6], vii., 504 and 526) pointed out that Stas made an error in calculating his own data. Stas obtained 32·074, but 32·06 is correct.

The work of the predecessors of Stas is now of historical interest only, and does not merit detailed criticism; in recent times the atomic weight of sulphur has rested chiefly upon the experiments of the famous Belgian.

Stas converted silver into its sulphide by heating it in a current of sulphur vapour or hydric sulphide, but because he did not know the precautions necessary for preparing perfectly pure silver (Dumas, *Ann. Chim. Phys.*, 1878, [5], xiv., 289; Richards and Wells, *Publication* No. 28, 1905, p. 66), it is evident that all of his work in which silver was weighed needs revision. Stas also reduced argentic sulphate to silver in a current of hydrogen, but in this case he did not take the very important precaution of fusing the sulphate before weighing (Richards, *Proc. Amer. Phil. Soc.*, 1903, xlii., 28), and, moreover, the possibility that the reduced silver might contain argentic sulphide or sulphate was by no means excluded.

A brief review of subsequent work may not be out of place, although it is of a different order of precision. Cooke reduced argentic sulphide in a current of hydrogen, and concluded that the atomic weight of sulphur must lie between the limits 32·14 and 31·98. In summing up his results he stated that "this is equivalent to confirming the accepted value of this constant, so far as any experiments on a scale less extensive than those of Stas can be of value to this end" (Cooke, *Proc. Amer. Acad.*, 1878, xiii., 52).

The determination of the atomic weight of sulphur by Richards was made incidentally in his work on the atomic

* *Publication* No. 69, Carnegie Institution of Washington.

weight of copper. The ratio $Na_2CO_3 : Na_2SO_4$ gave as a result S = 32·075. If sodium is taken as 23·008 instead of 23·053, the result becomes S = 32·043. No very great confidence was placed in these results at the time, as is shown by the following sentence :—"The results are hardly capable of deciding the present uncertainty in the atomic weight of sulphur" (Richards, *Proc. Amer. Acad.*, 1891, xxvi., 269). It is probable that the result is too low, as no proof could be obtained of the thorough desiccation of the sodic carbonate.

Very recently numerous atomic weight determinations have appeared, depending on a purely physical method, based on the assumption that Avogadro's hypothesis and the simple gas law PV = RT is strictly true for gases when infinitely expanded. Since it is impossible to determine the ratios of the densities of gases with sufficient accuracy at very low pressures, it is necessary to determine this ratio under normal conditions, and apply a different correction in each case, depending on the deviation of the gas from the simple gas law. It is probable that the ratio of the densities can be, and in most cases has been, determined with sufficient percentage accuracy. On the other hand, the correction is hypothetical and much less certain, and, accordingly, the method has but little value when the correction is large.

According to Leduc the ratio between the densities of sulphur dioxide and oxygen is 2·04835 (*Comptes Rendus*, 1894, cxvii., 219). If no correction is applied for the imperfection of the gases, this value leads to 33·55 for the atomic weight of sulphur. The correction in this case is unusually large, and therefore must be known with a high percentage accuracy if the result is to have any value as a determination of atomic weights. The following are the general methods of calculating the correction, but none seems to be of sufficient value for the present case.

The first, called the "method of corresponding states," was developed for this purpose by Leduc (*Ann. de Chim. Phys.*, 1898, [7], xv., 5). It depends on the assumption of Van der Waals that two gases are in corresponding states, and deviate equally from the hypothetical perfect gas if their temperatures and pressures are equal multiples or sub-multiples of their critical temperatures and pressures respectively. In calculating the correcting factor, the compressibility and critical constants are used. Leduc (*Ann. Chim. Phys.*, 1898, [7], xv., 94) by this method obtained 64·056 as the molecular weight of sulphur dioxide, and 34·071 as the molecular weight of hydrogen sulphide, and hence from both S = 32·056.

The second method is the "method of critical constants" as developed by Guye (*Comptes Rendus*, 1904, cxxxviii., 1215; *Bull. Soc. Chim.*, 1905, [3], 5 Août; *Journ. Chim. Phys.*, 1905, iii., 321). The correction is calculated by the use of Van der Waals's equation, the quantities *a* and *b* being calculated from the critical constants of the gases under consideration. In a complicated manner Guye applied a correction to the quantities *a* and *b* of Van der Waals's equation, because they appeared to vary slightly with the temperature and the pressure (Guye, *Bull. Soc. Chim.*, 1905, [3], 5 Août, p. 12), and in this way was obtained the value 64·065 as the molecular weight of sulphur dioxide; hence, S = 32·065.

The third method is called the "method of limiting density." It was originated by Daniel Berthelot in 1898 (*Comptes Rendus*, 1898, cxxvi., 954, 1030, 1415, 1501; *Journ. de Phys.*, 1899, [3], viii., 263), and has been used by Rayleigh (*Phil. Trans.*, A, 1901, cxcvi., 205; 1902, cxcviii., 417; 1905, cciv., 352) and Jaquerod (Jaquerod and Pintza, *Comptes Rendus*, 1904, cxxxix., 129; Jaquerod and Scheuer, *Comptes Rendus*, 1905, cxl., 1384). It depends on the experimental determination of the compressibilities of gases at pressures in the neighbourhood of one atmosphere. By an extrapolation the "limiting ratio" of the densities at very low pressures can be calculated. This method has reached its greatest perfection in the hands of Lord Rayleigh, who has shown that for the permanent gases the deviation from Boyle's law only varies slightly with the pressure, and therefore the extrapolation is fairly safe. This physical method has been applied with the greatest success to the cases of hydrogen, carbon, and especially nitrogen, because in these caees the correction is comparatively small. Here, also, however, the application to sulphur is far less satisfactory. It is to be regretted that Lord Rayleigh's work did not include compounds of this element.

Jaquerod and Pintza determined the density of sulphur dioxide at 760 mm., 570 mm., and 380 mm. pressure, and from these results calculated the compressibility. The results were extrapolated to zero pressure on the assumption that the deviations from Boyle's law diminish as the pressure is lowered. They obtained 32·01 as the atomic weight of sulphur. Afterwards Jaquerod and Scheuer determined the compressibility of sulphur dioxide through the ranges 400 to 800 mm. and 200 to 400 mm. by a method similar to Lord Rayleigh's. They found, as was to be expected, that the deviation from Boyle's law was smaller at the lower pressure. Nevertheless, in calculating the molecular weight of sulphur dioxide, they assumed that the deviation from Boyle's law per centimetre of pressure between 0 and 760 mm. was the same as between 400 and 800 mm. They obtained 64·036 for sulphur dioxide, and hence S = 32·036. If their measurement of the compressibility through the range 200 to 400 mm. is used, the result becomes 32·052, and it seems probable that yet a higher value is the true outcome of their experiments. These different conclusions emphasise the uncertainty of the method.

Probably the adsorption of sulphurous oxide and hydric sulphide on the glass of the containing globes introduces an error in both the density and compressibility determinations, and hence in facts to which the assumption above mentioned are applied. This possibility of adsorption seems to have been not sufficiently heeded by any of the experimenters on sulphur compounds. It adds yet another uncertainty to the results.

The upshot of these considerations is the conclusion that none of the work heretofore done upon the atomic weight of sulphur decides its value. Hence further investigation is imperative. The problem, for complete solution, must be approached from many sides, and the work must involve many compounds of sulphur. The following contribution describes one section of a comprehensive programme by which it is hoped the question may be answered.

Preliminary Experiments.

The sulphate of silver was selected as the most suitable starting-point for the present investigation, because it seemed probable that this salt could be prepared in a pure condition and accurately analysed. A further reason for studying argentic sulphate lies in the possibility of later combining the results with some ratio involving the sulphide and thus furnishing evidence on the even more important question as to the atomic weight of silver. Balanced against the advantages is the disadvantage that only about 10 per cent of its weight is sulphur, causing the experimental errors to be greatly multiplied in the calculations, but the advantages more than outweigh the disadvantage.

A tentative preliminary plan of operations was to fuse argentic sulphate in a platinum crucible, dissolve it, precipitate as chloride, and collect and weigh the precipitate. This plan was thwarted by numerous obstacles. It was found that the sulphate decomposes slightly when fused, a difficulty which was later overcome. Again, the quantitative solution of the silver sulphate was a very tedious process. Eight grms. fused in a platinum crucible and placed in 1·5 litres of water required six weeks for its complete solution, even with frequent agitation. The action on the glass during this long time, the danger of the access of gaseous impurity, and the loss of valuable time all made this difficulty a serious one.

Argentic sulphate can be readily dissolved by placing twice its weight of concentrated sulphuric acid in the

crucible, and heating at about 300°; on cooling, the acid sulphate of silver crystallises out (Schultz, *Pogg. Ann.*, 1868, cxxxiii., 143). Upon adding water to this acid sulphate the normal sulphate is formed as a fine powder, which can readily be washed into the precipitating flask, and dissolved. The large excess of sulphuric acid thus introduced was far from desirable, however, for it tends to cause considerable occlusion of argentic sulphate in the precipitated chloride. In order to test this question, a solution, prepared as described above, and containing 7·4 grms. of argentic sulphate, was precipitated with hydrochloric acid. The precipitate was washed by decanting eleven times with very dilute hydrochloric acid, and then dissolved in ammonia and diluted. The argentic chloride was then re-precipitated with hydrochloric acid; the solution should contain all the sulphate previously occluded. After settling, this mixture was filtered, and the perfectly clear solution was evaporated in a platinum dish over an alcohol lamp until ammonic chloride crystallised out on cooling, the volume being then about 0·1 litre. To this were added about 10 grms. of baric chloride. An undoubted precipitate of baric sulphate was produced, which proved that there is considerable occlusion of sulphate by argentic chloride precipitated from solutions containing a large excess of sulphuric acid.

For the sake of comparison, approximately the same amount of argentic chloride prepared from nitrate was dissolved in ammonia, and 3·5 mgrms. of sulphate added. The solution was treated exactly like the preceding operations, and yielded about the same amount of precipitate. This experiment gives an approximate idea of the extent of the occlusion.

In searching for a means of wholly eliminating the sulphate it was found that a small proportion of argentic sulphate in argentic chloride could be completely converted into chloride by fusion in a current of hydrochloric acid gas. This observation led to the development of a new process in which the entire reaction was carried out in this manner, fused argentic sulphate being wholly converted into chloride without the need of dissolving in water. Thus the operation was greatly simplified, and the chances of error diminished.

The method of preparing the materials, the shape and nature of the apparatus, and many of the precautions and details of manipulation were adopted only after numerous preliminary experiments. A detailed account of this tentative work is, however, unnecessary, since the important results are implied in the description of the method which was finally adopted.

The Preparation of Pure Materials.

Sulphuric Acid.—The best commercial "chemically pure" acid was twice fractionally distilled, using a quartz condenser and a platinum dish as receiver. Only the middle fractions were used; 17 grms. left no visible or weighable residue on evaporation.

Argentic Sulphate.—Pure argentic chloride residues from previous atomic weight investigations in this laboratory were reduced with invert sugar and sodic hydrate. The reduced silver was thoroughly washed and dissolved in nitric acid, and the nitrate was diluted and filtered. It was evaporated on the steam-bath until saturated, and crystallised by adding an equal volume of concentrated nitric acid and cooling. The crystals were drained centrifugally as usual (Richards, *Journ. Am. Chem. Soc.*, 1905, xxvii., 104). The crystallisation from pure concentrated nitric acid and centrifugal draining was repeated five times, using Jena glass vessels. It was finally re-crystallised once more, using a platinum dish and re-distilled nitric acid. This silver nitrate was dissolved in a small amount of water in a platinum dish, and an excess of the purest sulphuric acid, diluted with an equal volume of pure water, was poured into it. The precipitated silver sulphate was drained in the centrifugal machine. It was then dissolved in hot concentrated sulphuric acid in a platinum dish, and the solution was boiled for several minutes to expel nitric acid. On cooling, the acid sulphate crystallised in large crystals. This acid sulphate was very thoroughly whirled, placed in a platinum dish, and treated with purest water. Heat was evolved, and the normal sulphate crystallised out as a fine powder. This powder was washed by decantation with the purest water until the wash-waters were no longer acid. (Unless this precaution is taken the silver sulphate cannot be dried thoroughly in the air-bath; in which case it would be impossible to clean properly the receiving end of the tube into which it was afterwards introduced; see below). All the water used in this work was purified in the manner described in previous communications. During this washing the action of light on the wet silver sulphate produces a slight violet colour. This, however, does no harm, as any slight decomposition is remedied during the subsequent fusion. It was then dried as much as possible in the centrifugal machine, and the drying was completed in an air-bath at 110°. These operations were carried out as much as possible under the protection of a very large inverted funnel, and the dish was kept covered with a large watch-glass, to avoid the introduction of dust. This sample was called A, and was used in the preliminary series, and in Experiments 4 and 5 of the final series of quantitative experiments.

Sample A was dissolved in concentrated sulphuric acid, boiled, crystallised as acid sulphate by cooling, centrifugally drained, converted into the normal sulphate by adding water, washed, and dried as before. This sample was called Sample B. Since the mean of the results with this sample is the same as the mean of Experiments 4 and 5, in which Sample A was used, it is evident that the boiling of the sulphuric acid solution followed by a crystallisation in two different crystalline forms did not affect the result; therefore further purification seemed unnecessary.

Hydrochloric Acid.—Hydrochloric acid, which was only used as a gas, was made from two sources. In Experiments 5 and 6 the hydrochloric acid was made by dropping pure sulphuric acid on pure ammonium chloride. In the other experiments the best commercial concentrated hydrochloric acid was used. Richards and Wells (*loc. cit*) have shown that this acid contained no other halogen or arsenic; it was therefore suitable for our purpose.

The Fusion of Argentic Sulphate.

Much thought was expended on the devising of a piece of apparatus which should be suitable not only for the fusion of argentic sulphate, but also for the quantitative conversion of the sulphate into the chloride. Finally, the simple symmetrical tube shown in Fig. 1 was found to be

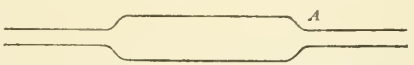


Fig. 1.—Quartz Tube used to contain the Argentic Salts. (One-half actual size).

best. It was the outcome of several trials and suggestions, and consisted of a thin cylindrical tube of fused quartz with smaller quartz tubes fused upon the ends. (We are greatly indebted to Prof. Baxter for his kindness in making this apparatus from a fine quartz tube and a quartz test-tube. To Mr. F. B. Coffin also we are indebted for a suggestion which led to a modification of the original shape of the tube). The tube was very light, weighing less than 6 grms. A very fine platinum-wire was wrapped many times around the constricted portion of the tube (A); by pulling this the tube could be readily rotated. It was hung on the balance in a horizontal position by means of a platinum-wire. The same tube was used throughout the research, the cylindrical shape giving it sufficient strength to withstand all the strains to which it was subjected.

The tube remained remarkably constant in weight in spite of the very vigorous treatment it received. During the entire fifteen experiments the loss in weight was only 0·41 mgrm., and during the twelve experiments of the final

series the loss was only 0·16 mgrm. This slight loss is probably accounted for by a slight solubility of the quartz in the concentrated ammonia or potassic cyanide solution used to remove the argentic chloride after each determination.

The sulphate of silver prepared as described above must have contained a little included water and excess of sulphuric acid, since it had been crystallised from an acid solution (Richards *Proc. Amer. Phil. Soc.*, 1903, xlii., 28). The only certain method of removing mother-liquor included within crystals is to fuse the salt. This part of the problem caused considerable difficulty; for it was found that argentic sulphate decomposes slightly when fused in air, becoming yellowish brown in colour. In order to decrease this thermal dissociation, the experiment was made of fusing the salt in a current of dilute sulphuric oxide, with complete success. The salt is then pure white in colour.

The small crystals of argentic sulphate were pushed into the tube with a platinum rod, and the narrow ends were freed from loosely adhering argentic sulphate by means of a clean feather tip, which had been previously washed with alcohol and ether to free it from grease. The tube was supported, on hooks of hard glass, in front of the apparatus for delivering sulphur trioxide. The very fine platinum-wire needed for rotating it had been wound around the tube in the first place.

The apparatus for delivering a current of pure dry air or sulphur trioxide or hydric chloride is shown diagrammatically in Fig. 2. A current of air was first driven over red-hot copper oxide (A) to remove organic matter, and subsequently through an Emmerling tower (B) containing beads moistened with a strong caustic potash solution. This tower was closed by a rubber stopper at the top, which introduced no impurity, since nothing but pure air passed over it. From this point, however, the apparatus contained no rubber connections or stoppers. All stopcocks were lubricated with phosphoric or sulphuric acid.

The air was dried by passing through two Emmerling towers (C and D) containing beads moistened with concentrated sulphuric acid. The current of air could then be either used in a pure dry state by passing through L or F, or else charged with sulphur trioxide by bubbling twice through fuming sulphuric acid in the bottle E. This acid was kept saturated by an excess of solid sulphur trioxide. A current of air mixed with any desired proportion of sulphur trioxide was thus delivered through G into the quartz tube H. The delivery tube, G, and the quartz tube, H, touched each other, but no attempt was made to secure a tight joint.

The argentic sulphate contained in the quartz tube was then fused with a fish-tail Bunsen burner held in the hand. A red heat is required. When all of the sulphate was fused, the stopcock, P, delivering sulphur trioxide was closed, and a rapid current of air was admitted through F. As soon as the fumes of sulphuric acid could no longer be seen escaping from the end of the quartz tube, the flame was removed, and the tube was slowly rotated by drawing out the platinum-wire wrapped around one end. This causes the argentic sulphate to solidify in a thin sheet around the tube. Unless care is taken to keep the salt at least 1 cm. distant from either of the end tubes, difficulty is experienced during the conversion into chloride.

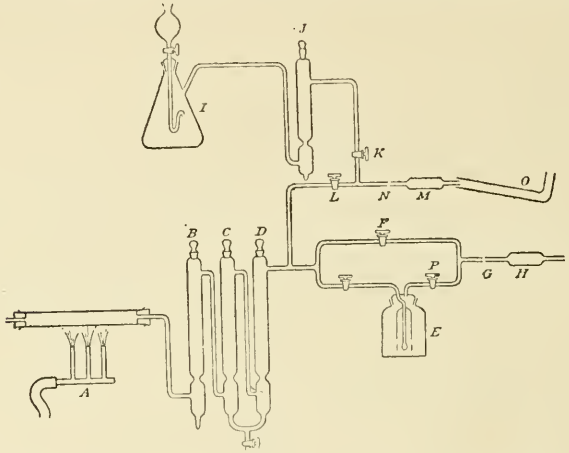


Fig 2.—Apparatus for Delivering appropriate Gases into the Quartz Tubes.

The final solidification in the current of pure dry air was carried out very rapidly, in order to avoid decomposition and obtain a perfectly white sample. If the argentic sulphate was kept fused ten or fifteen seconds too long after the sulphur trioxide current was stopped, a yellowish brown product was obtained. This indicates that the salt contained either metallic silver or argentic sulphide. Richards, Wells, and Forbes have shown that a slight discolouration of a fused silver salt is a very delicate test for impurity (Richards and Wells, *Carnegie Inst. Pub.* 28, 1905, xxviii., 31; Richards and Forbes, *Carnegie Inst. Pub.* 69, 1907, p. 55). The loss of weight due to this discolouration was very slight, as will be shown below.

The entire tube was later heated in a current of pure air at a temperature above the boiling-point of sulphuric acid for about five minutes, in order to drive out any possible accidental trace of acid in the tube. While still warm it was placed in a desiccator, and later weighed. The tube was kept horizontal until the end of the experiment, to avoid any chance of mechanical loss.

The device of spreading the salt in a thin layer around the tube by rotating the tube during the cooling had four very important advantages:—First, the chance of breaking the very fragile quartz tube during the solidification and cooling was greatly reduced by the more even distribution

of the strain; secondly, the salt was agitated and spread out in a thin layer while still fused in a current of pure air, thus facilitating the escape of any possible trace of dissolved sulphur trioxide; thirdly, the cooling was made more uniform and rapid, so that the argentic sulphate had no time to decompose before it had solidified; and fourthly, a much larger surface was exposed to the later action of the hydrochloric acid.

The possibility just mentioned that the colourless argentic sulphate might contain an excess of sulphur trioxide needed careful consideration. Unfortunately, a direct test for acid seemed to be impracticable, owing to the slight solubility of silver sulphate; hence light upon the question was sought in several distinct ways.

Weber (*Ber.*, 1884, xvii., 2503) has found that in order to prepare a compound $Ag_2S_2O_7$ argentic sulphate must be heated with sulphur trioxide under pressure in a sealed tube. This, together with the fact that argentic sulphate decomposes so easily when fused, indicates that it does not have a great tendency to retain sulphuric oxide, and that the vapour tension of the trioxide in the disulphate is far above that maintained in the present experiments. In order to obtain quantitative evidence, the pure white sulphate in six of the final experiments, after being weighed, was fused again for about ten to fifteen seconds in order to decompose it slightly. This gave a slight but unmistakable dark colour to the salt. The resulting losses of weight are here tabulated:—

The Loss of Weight caused by slight Decomposition.

Experiment No.	White Ag_2SO_4.	Darkened Ag_2SO_4.	Difference.
9.	5·27714	5·27709	0·00005
10.	5·16313	5·16302	0·00011
11.	5·08383	5·08377	0·00006
12.	5·13372	5·13367	0·00005
13.	5·16148	5·16138	0·00010
15.	5·37436	5·37425	0·00011
		Average	0·00008

The loss in weight was thus on the average only 0·08 mgrm. or 0·0015 per cent. It seems certain that at least part of this loss in weight was due to a deficiency of either oxygen or sulphur trioxide in the darkened sulphate, and not to the loss of an illegitimate excess of the latter substance. Therefore, although it may be a debatable question as to whether it is safer to take the weight of the white or darkened samples as the true weight, it seems probable that the weight of the white sample was more trustworthy. Even at the worst the uncertainty cannot have been greater than 0·001 per cent. This result agrees with the earlier conclusions already cited concerning the obvious effect of very slight decomposition on the colour of silver salts. It appears that in the present case, as in the others, the slight stability of these compounds is a real assistance in the production of a typical compound, instead of a hindrance to precise quantitative work.

For weighing the argentic sulphate, and of course the chloride also, the Troemner balance which had served in many similar researches was used (Richards, *Proc. Amer. Acad.*, 1891, xxvi., 242). The Sartorius platinised brass weights were standardised by the usual Harvard method (Richards, *Journ. Am. Chem. Soc.*, 1900, xxii., 144).

As usual, all weighings were made by substitution, a make-weight being placed on the right-hand balance pan. In order to avoid as far as possible any error due to changing meteorological conditions, a substituting counterpoise of the same material and approximately the same surface and weight was used. Every weighing was repeated, and the successive values seldom differed more than 0·03 mgrm. No difficulty was experienced from hygroscopic adsorption of water by either argentic sulphate or argentic chloride, except on a few days when the air was unusually humid. In these cases the tube was heated to about 330°, and allowed to remain in a desiccator until the conditions were more favourable. The tube was always allowed to remain at least three hours in a desiccator near the balance before making a weighing, and during this time was covered by a black cloth to protect the sensitive salts from the light.

In order to correct the weights to the vacuum standard, the specific gravity of argentic sulphate is needed. Following are the published results concerning this datum:—

Density of Argentic Sulphate.

Karsten (*Schweigger's Journ.*, 1832, lxv., 419) ..	5·341
Playfair and Joule (*Mem. Chem. Soc.*, 1845, ii., 430)	5·322
Filhol (*Ann. Chim. Phys.*, 1847, [3], xxi., 417) ..	5·410
Schröder (*Pogg. Ann.*, 1859, cvi., 245)	5·425
Petterson (*Upsala Nova Acta*, 1874, [3], ix., 35)..	5·49 5·54

After a study of the original papers, the value 5·45 was provisionally adopted as the most probable value, but, as there was some doubt about its accuracy, this was verified by experiment.

The density of the toluol to be displaced by the salt was determined by means of an Ostwald pycnometer at 29·2° to be 0·8566 (the mean of three concordant determinations); 6·067 grms. of previously fused silver sulphate were found to displace 0·9532 grm. of this toluol, and therefore occupied 1·113 millilitres (the mean of two determinations). Hence the density of argentic sulphate is 5·45, as supposed. This involves an additive correction of 0·0000775 grm. to each apparent grm. of the salt, a value which is decreased 0·0000011 by an increase of a centimetre of atmospheric pressure, or decreased 0·00000026 by an increase of a degree of temperature. The correction to the weight was applied accordingly.

(To be continued).

THE

USE OF FELSPATHIC ROCKS AS FERTILISERS.*

By ALLERTON S. CUSHMAN,
Assistant Director, Office of Public Roads, and Collaborator, Bureau of Plant Industry.

Introduction.

In view of the great demands that are being made upon the agricultural resources of the country, it is a matter of vital importance that consideration be given to the available supplies of elements which are necessary to sustain and maintain the quality and quantity of the crops. It is well known that there are three principal fertilising materials—nitrogen, phosphoric acid, and potash. The discovery of electro-chemical and bacteriological processes for fixing the nitrogen of the air, thereby changing it into a form in which it can be used as a plant food, seems to remove all doubt as to the abundance of the supply of this important element for all time to come. An enormous geographical area of this continent is underlain with practically inexhaustible supplies of phosphatic rock, which, with the phosphates obtainable in waste bone, slaughterhouse tankage, fish scrap, and the basic slags from the iron industry, insure a limitless supply of phosphoric acid.

With regard to potash alone there has been reason to feel anxiety. Up to the present time no deposit or source of this necessary element in any of the forms in which it has been heretofore considered available as a plant food has been discovered or developed in this country. The mines of Stassfurt, Germany, furnish almost the entire supply of potash for fertiliser in the United States, exclusive of that which is used over and over by the processes of natural and green manuring. The potash salts which up to this time have been exclusively used for fertilising consist of muriate, sulphate, nitrate, and carbonate, either in a crude or in a previously purified condition. Kainite

* From *Bulletin* No. 104, U.S. Department of Agriculture, Bureau of Plant Industry.

TABLE I.—*Imports of Potash Salts for Use as Fertilisers.*

(Compiled from data furnished by the Bureau of Statistics, U.S. Department of Agriculture).

Kind of fertiliser.	1903.		1904.		1905.	
	Weight (lbs.).	Value (dols.).	Weight (lbs.).	Value (dols.).	Weight (lbs.).	Value (dols.).
Crude carbonate ..	11,130,789	141,033	8,193,872	224,396	7,166,569	218,816
Crude muriate . ..	172,838,780	2,630,457	161,503,735	2,428,480	202,366,601	3,241,152
Crude nitrate	11,946,685	320,082	16,727,175	433,626	14,512,306	386,098
Crude sulphate . ..	45,156,964	782,082	47,592,131	833,954	54,577,670	958,305
Kainite	553,875,840	1,080,393	356,124,160	839,382	539,369,488	1,143,296
Total	794,949,058	4,954,047	590,141,073	4,759,838	817,992,634	5,947,667

is a trade name given to a crude product of the German mines which contains about 13 per cent of actual potash, largely in the forms of sulphate and chloride (muriate). The quantity and value of potash salt to be used as fertilisers imported in the fiscal years 1903, 1904, and 1905 are shown in Table I. The price of the potash unit has shown a tendency to increase each year.

All of the above salts of potash are readily soluble in water, and therefore become quickly available as plant food when applied as fertilisers. On the other hand, the acids with which the potash is combined in these salts, especially in the cases of the sulphate and chloride, are absorbed only in extremely minute quantities by growing plants. The natural consequence of this is that, as the potash is taken away year after year, the acid elements collect, in some cases to the great detriment of the soil.

Potash in some form is absolutely necessary to the successful growth of all crops, and is found in varying degrees in the ashes of wood and of vegetable growths of all kinds. This is illustrated in Table II., in which analyses of ashes of a number of vegetables are given. It must be remembered, however, that the amounts of this element found in the ashes of plants vary greatly under different conditions, and that the sap of plants frequently absorbs much more of a given element than is actually necessary for its growth. The important point is that potash is an essential plant food of all crops, and particularly of those species which are starch builders.

TABLE II.—*Analyses of Vegetable Ash.*

Ash.	Phosphoric acid, P_2O_5.	Potash, K_2O.	Soda Na_2O.
	Per cent.	Per cent.	Per cent.
Pea	36	40	1
Bean	30	44	1
Potato	19	59	2
Parsnip	18	36	5
Carrot	12	36	3
Cabbage	16	48	4
Turnip	13	39	5
Artichoke	16	65	2
Tobacco	15	49	11

We can trace the source of potash in all its forms and wherever found to the igneous rocks which constituted the original crust of the earth. From the averages obtained from the analyses of a large number of crystalline rocks of common occurrence found in this country, Clarke (*Bull.* 228, U.S. Geol. Survey, p. 20) has made the following calculations of the relative abundance of various rock-forming minerals :—

	Per cent.
Apatite (phosphate of lime)	0·6
Titanium minerals (oxides and silicates)	1·5
Quartz (silica)	12·5
Felspar (silicates of aluminium, potash, soda, and lime)	59·0
Biotite mica (silicates of aluminium, magnesium, potash, &c.)	3·8
Hornblende and pyroxene (complex silicates) ..	16·8
Miscellaneous	5·8
Total	100·0

It is seen from this that probably the majority of all the original rocks contain more than 50 per cent of felspar. There are, however, a great many different varieties of felspar. The felspars belong to a type of minerals known as silicates, in which aluminium and other elements, such as potash, soda, and lime, are combined with silica. Pure orthoclase felspar is a silicate of aluminium and potash, which theoretically should contain 16·8 per cent of potash(K_2O). As a matter of fact, it is extremely difficult to find an example of pure orthoclase, and in most of the felspars, which occur in large deposits, the potash is to a greater or less extent replaced by soda or lime, or both. For this reason it is impossible to tell without a chemical analysis how much potash any given felspar will contain. The granite rocks consist of felspar, quartz, and a little mica in varying proportions; many of the other well-known rocks, such as the slates, sandstones, gneisses, and traps, also frequently contain more or less felspar. Some of these rocks carry little or no potash, although many of them will run as high as 5 per cent; very few of them run higher than this.

A cubic foot of granite weighs about 170 pounds; on a 5 per cent basis, 8·5 pounds of this is potash. A quarry 100 feet square and 100 feet in depth of such rock would therefore contain 8,500,000 pounds of potash (K_2O). It is at once apparent that nature offers a limitless supply of raw material which only awaits an economical process to make the potash available.

In many localities there occur large dikes or deposits of more or less pure felspars, which usually run higher in potash than the true granite rocks. These large deposits, which occur in a great many of the States, have been developed in Maine, Connecticut, Pennsylvania, New York, and Maryland, where they have been mined extensively and the felspar ground to fine powder, principally for use in potteries. As has been said, pure orthoclase felspar should contain 16·8 per cent of potash (K_2O), but none of these deposits will run on the average much more than 8 to 10 per cent. For pottery use it is essential that the spar should melt in a kiln fire to a clear white glass, and it must therefore be almost entirely free from mica or iron-bearing minerals. For this reason there are large quantities of materials at every felspar quarry which, though unfit for pottery use, would be valuable if any method were known of making potash available.

The question whether fine-ground felspar can be used as a potash fertiliser has been a matter of controversy for many years. There is a large and widely scattered literature on the subject, an examination of which shows that the matter has been debated with much vigour, and sometimes with prejudice and intolerance on both sides. It is easy to find the published records of a number of experiments, made by trained and thoroughly competent agriculturalists, which tend to show that ground felspar is an efficient potash fertiliser. On the other hand, a number of experiments seem to indicate that the potash is only slightly available while others would appear to show that the ground rock is entirely useless. On account of the large interests involved in the settlement of this question it is not difficult to see why vigorous differences of opinion, and even unjust prejudice, should have arisen. When, however, trained investigators reach opposite conclusions,

based upon experimental evidence, we are forced to the opinion that while ground felspar may be a useful fertiliser under certain conditions it is not so under others.

It is the object of this *Bulletin* to present and discuss as fully as possible all the evidence that can be obtained on both sides of this important question. The great demand for information on the subject which has arisen and the numerous misstatements that have been printed make it desirable to present the evidence obtained up to date, even though many more years will be necessary for the conclusion of careful systematic investigation under crop and field conditions.

The availability of potash contained in felspathic rock must depend upon several important considerations, which can best be expressed by a discussion of the following questions :—

1. Is the potash locked up in felspar and the felspathic rocks, such as granite, gneiss, rhyolite, syenite, &c., to any extent available as a fertiliser when these rocks are crushed or ground to fine powder ?

2. If the first question can be answered in the affirmative, what influence does fineness of grinding have on the question, and to what degree of fineness is it necessary to grind in order to make a sufficient amount of potash available in the first season after application ?

3. What would be the cost of using ground rock in place of the soluble compounds which up to the present time have been exclusively used, and would there be economy in so doing ?

4. Could any subsequent damage result from the use of ground rock ; and if so, how would such damage compare with that which follows the continued use of soluble compounds, such as chloride, sulphates, and carbonates ?

5. If it should be determined that the potash in ground felspathic rock is only partially available as a fertiliser, is there any method or process by which the ground rock could be treated so as to increase this availability ?

(To be continued).

SYNTHETICAL CHEMISTRY IN ITS RELATION TO BIOLOGY.*

By Prof. EMIL FISCHER, F.R.S.

Exactly forty years are elapsed since Faraday's death, and already, on eight occasions, discourses in honour of his memory have been delivered, at the instance of this Society, by distinguished representatives of the sciences which he did so much to forward. Most of them, mindful of Faraday's discoveries, have dealt with general problems connected with our fundamental conceptions of matter and its inherent forces, so that, when honoured with the invitation to deliver the ninth of these lectures, I could not but feel sensible of the difficulty of following the example of my predecessors, as the field in which I have sought to enlarge the boundaries of knowledge is one far removed from such considerations.

In Faraday's time, it is true, the labours of workers in the natural sciences were not specialised as they are now ; his genius was such, however, that, although not trained in its service, he was able to enrich organic chemistry with observations of momentous consequence. I need but allude to his discovery of benzene : the practical importance of this substance and its dominant position in the host of carbon compounds with which we are now acquainted were generally recognised in the course of the celebration held in this room, only fifteen months ago, in honour of Sir William Perkin.

But in the course of his labours as an investigator Faraday never approached the attractive problems which organic chemistry affords on its biological side. I must therefore crave your indulgence in selecting this theme in particular as the subject of my address. Happily, I am sustained by the conviction that biology, on account of the breadth and importance of its aims, may claim to rank with the inorganic sciences, although perhaps it lacks their exactness of method ; nowhere can it count on fuller recognition of its achievements and of the importance of its problems than among the countrymen of Charles Darwin.

It is easy to understand why in its early youth organic chemistry was so closely connected with biology ; the materials which the chemist was called upon to investigate were mostly products of animal or vegetable origin. Indeed, carbohydrates, proteins, and vegetable acids served Lavoisier, Gay-Lussac, Berzelius, and Liebig as materials in elaborating the methods of elementary analysis.

The isolation of urea from animal urine by Rouelle, the recognition of uric acid, lactic acid, malic acid, and glycerin by Scheele, the isolation of asparagin by Vauquelin and Robiquet, of morphine by Serturnier, together with many other similar discoveries accomplished during the first ten years of the nineteenth century, are admirable examples of the manner in which the living world was drawn upon and made to yield up its treasure of chemical compounds. The many hundreds of natural organic compounds enumerated in the text-books of animal and vegetable chemistry are proof of the rich harvest since gathered in this field of investigation. But how small is their number when compared with the 130,000 carbon compounds which organic chemistry can boast of to-day. All these, it is known, are either products of the artificial transformation of organic matters occurring naturally or have been completely synthesised from their elements. The accumulation of this huge material, including the elaboration of the necessary methods, has been the main occupation of organic chemists during the past sixty years ; and as their discoveries gave rise to much happy speculation, for the time being they took the lead in developing chemical theory.

It is not to be denied that, in the latter half of the last century, owing to the growth of the subject in importance, organic chemistry became separated from biology. It cannot be mere chance that the most famous of Liebig's pupils, A. W. Hofmann, A. Kekulé, and A. Wurtz, did not follow the example of their great teacher, whose chief triumphs were won by the use he made of chemical methods in solving biological problems. Perhaps they were restrained by the feeling that, mainly through his influence, physiological chemistry had been developed into a separate discipline, which should be cared for by men who could devote themselves entirely to its service. Such subdivision of labour undoubtedly has many advantages ; the disadvantages would have outweighed these had it precluded interchange of experiences and friendly co-operation of workers in the two fields ; the history of both sciences, however, affords ample proof that such has not been the case.

Physiologists have ever been ready to avail themselves of the latest developments of chemical analysis and synthesis, whilst organic chemists have not only been stimulated in many ways by biologists, but their studies have derived much practical aid from biological science. I may instance the modern development of the chemistry of fermentation, which began with the pioneer work of Pasteur and was greatly favoured by the introduction of Koch's refined bacteriological methods ; also the flourishing industry to which the manufacture of medical remedies prepared by synthetic methods has given rise.

But organic chemistry will certainly never be content to act as the mere handmaid of biology. This is impossible, as the theoretical and technical problems which she is already called upon to consider are too numerous and they cannot fail to increase in number and importance in the future. But I do consider it not only possible but desirable, that the close connection of chemistry with biology which

* Faraday Lecture, delivered before the Chemical Society, October 18, 1907. From the *Transactions of the Chemical Society*, 1907, vol. xci.

prevailed in the days of Liebig and Dumas should be re-established, as the great chemical secrets of life are only to be unveiled by co-operative work. I will therefore attempt to indicate the part chemistry can play by references to cases of which I can claim to have personal experience.

We know that in nature the construction of organic matter begins in the leaves of plants with the conversion of carbon dioxide into sugar, from which many physiologists suppose the complex substances contained in the living cell are formed by further changes in which nitrogen, sulphur, and phosphorus take part.

These transformations are for the most part enveloped in mystery. We know nothing definitely even of the assimilation of carbon dioxide. Of the various hypotheses advanced to explain the change, that advocated by A. von Baeyer has gained most support, namely, the view that the initial product is formaldehyde, glucose being formed from this by a process of polymerisation. Actually both changes have been effected artificially. After it had been shown by Butleroff that on heating formaldehyde with lime water a sugar-like, syrupy product is formed, and O. Loew had improved the method of effecting the condensation, I was able to adduce proof that the complex mixture contains a small quantity of an α-acrose which can be transformed into glucose. As it was known that carbon dioxide could be converted into formaldehyde by more or less drastic means, the preparation of glucose from carbon dioxide thus became a possibility. Recently, Fenton has succeeded in carrying out the reduction of carbon dioxide to formaldehyde at a low temperature in aqueous solution, so that it is now possible to effect the complete synthesis of sugar at temperatures such as prevail in the living plant. But how thorough is the work of the plant in comparison with our laboratory practice; usually when such questions are discussed, the poor yields which our methods give rise to are forgotten!

I need only allude here to recent apparently successful attempts, on the one hand, to effect the reduction of carbonic acid to formaldehyde by means of light and, on the other, to detect formaldehyde in green leaves, as Professor Meldola dealt exhaustively and critically with these questions in his Presidential Address eighteen months ago. I may be allowed, however, to dwell somewhat on one peculiar feature of the natural change, namely, the asymmetric character of the synthesis; according to present experience, and especially the brilliant investigations of H. Brown and Morris, the optically active hexoses of the *d*-series, glucose and fructose, are alone formed.

But from the experience gained in effecting syntheses in the sugar group, as I showed some time ago, it is possible to give a fairly satisfactory explanation of this change. It is only necessary to assume that the condensation is preceded by the formation of an additive compound of formaldehyde with some optically active constituent of the chlorophyll granules. I shall give a more precise form to this hypothesis if I say that I consider it probable that the carbon dioxide itself enters into combination in this manner, as there is reason to suppose that the proteins offer sufficient opportunity for its fixation; according to Siegfried, even the simple amino-acids are capable of combining with carbon dioxide. I am inclined to think that this compound with carbon dioxide undergoes decomposition into oxygen and a reduction product, probably a derivative of formaldehyde; the condensation to sugar takes place either in the original asymmetric complex or in one produced from it by a secondary change involving the separation of the formaldehyde and its re-association in some other manner. It may be that the condensation takes place directly or that intermediate compounds, biose or glycerose, are formed. Thanks to the researches of Marckwald and especially those of Mackenzie, we are acquainted with a whole series of asymmetric syntheses; no one of these, however, is half so complete as that involved in the formation of sugar under natural conditions. Indeed, it is obvious that if the natural process is to be imitated *in vitro*, it will be necessary to alter the methods hitherto adopted in every single detail; difficult as this may appear, it is not altogether impossible.

But even if this be done successfully, the precise nature of the assimilation process will not be finally elucidated. It is to be expected that this will only be accomplished when biological research, aided by improved analytical methods, has succeeded in following the changes which take place in the actual chlorophyll granules.

The carbohydrates elaborated by the plant undergo combustion to carbon dioxide and water in the animal body. The change is easily effected by means of powerful oxidising agents at the ordinary temperature; the natural process, however, must be a very different one, as in the organism oxygen is conveyed to the carbohydrate by oxidising enzymes and doubtless many intermediate products are formed of which we know little at present.

It would be easy to multiply examples. But these two are sufficient to demonstrate the incompleteness of the explanation of biochemical processes deduced from the data of organic chemistry. The service rendered to biology by chemical analysis and synthesis which will be rendered by it in even greater measure in the future, is to be sought in other directions.

The ultimate aim of biochemistry is to gain complete insight into the unending series of changes which attend plant and animal metabolism. To accomplish a task of such magnitude, complete knowledge is required of each individual chemical substance occurring in the cycle of changes and of analytical methods which will permit of its recognition under conditions such as exist in the living organism. As a matter of course, it is the office of organic chemistry, especially of synthetic chemistry, to accumulate this absolutely essential material. The chemical constitution of hundreds of carbon compounds which occur naturally has already been determined and their more important properties have been established. But far more remains to be done. In proof of this, let me briefly direct your attention to the three great classes of substances which predominate in the living world: the fats, the carbohydrates, and the proteins.

It was established at least ninety years ago by Chevreul, in the course of his celebrated investigations into the process of soap-making, that the fats can be decomposed into the glycerin discovered by Scheele and into fatty acids; but the relationship of these latter to one another could not be understood until the conception of homologous series had been evolved in organic chemistry. The classical researches of Berthelot and the discovery of glycol by Wurtz were necessary preliminaries to the establishment of the constitution of glycerin; the final proof that the fats are neutral glyceric salts of the fatty acids was first provided by Berthelot's synthesis. Synthetic methods have made us acquainted with the mono- and di-glycerides and also with mixed triglycerides such as have frequently been met with of late in nature.

Nevertheless, the group in which the natural fats are ranged is one in which there are still many lacunæ and many mis-statements to be corrected. Fatty acids of high molecular weight, which for years were regarded as entities, such as margaric acid, are now acknowledged to be mixtures; others, like the cerotic acid of bees-wax, have received new formulæ; in fact, the higher acids and the oxy-acids all require to be studied afresh, and, whilst it is true that the general constitution of the fats is known with certainty and the quantitative composition of the most important natural mixtures is established with a fairly satisfactory degree of accuracy, yet there is much uncertainty on the physiological side; even such an apparently simple problem as that involved in the determination of the manner in which fats are absorbed in the animal intestine has not yet been definitely solved. Although enzymes capable of cleaving fats are known to be present in the secretions of the stomach and pancreas, opinions are still divided as to whether the fat is absorbed

in a state of fine emulsion or whether it first undergoes hydrolysis.

Still less is known of the manner in which fats undergo combustion to carbon dioxide and water in the animal body. Hitherto this change has been imitated artificially only at relatively high temperatures. It is obvious that it would be of far greater interest to discover oxidising agents which would produce the effect at low temperatures. No doubt many intermediate products would be met with and the study of these would afford valuable assistance to biologists in devising experiments with animals.

The formation of fats in plant and animal tissue is no less complicated a phenomenon. It is certain that carbohydrates are the chief source of supply. We know next to nothing, however, of the actual course of this remarkable synthesis; it is easy to imagine that glycerol may be formed by the hydrolysis of glucose and that three molecules of glucose may give rise to an acid containing eighteen carbon atoms. But the process involved in the conversion of sugar which is rich in oxygen into fatty acids containing little oxygen remains wrapped in mystery. I imagine that this change, like that which attends alcoholic fermentation, is effected by a rearrangement of oxygen atoms within the molecule and that it involves the elimination of carbon dioxide. To imitate such a process artificially, of course, is an attractive problem to be dealt with from the synthetic side; but it is doubtful if it can ever be solved by purely chemical methods. In all probability, the organism has at its disposal for the purpose a number of enzymes which effect the complete synthesis in a series of interactions following rapidly one upon another.

The problems offered by the fats are simple, however, in comparison with those connected with the carbohydrates. The original subdivision of the group into mono-, di-, tri, and poly-saccharides has been justified in practice. Up to the present time only the monosaccharides have been studied satisfactorily from the point of view of their spatial structure. The dogma which at one time prevailed that Nature produces only carbohydrates with six atoms of carbon was upset by Kiliani's discovery that arabinose contains but five atoms of carbon. Since then the group of the mono-saccharides has been so extended by synthetic means that sugars of all types, from glycollic aldehyde (biose) to the nonoses, are now known, the group including besides the seven compounds which occur naturally no less than forty-five synthesised products.

Our knowledge of this group is also fairly satisfactory from the stereochemical standpoint, as the greater number of the isomerides predicted by theory as well as the more important aldohexoses and aldopentoses have been prepared and their inter-relationship can be expressed by steric formulæ. Similar results have been arrived at in the case of the great class of glucosides, the synthesis of the most simple representative from glucose and methyl alcohol having led to the discovery of both the theoretically possible stereoisomerides.

The growth of our knowledge of the monosaccharides has proved in many ways to be of importance in connection with biological inquiry, especially in enabling us to penetrate the mystery of enzyme action somewhat further.

On contrasting the effects which emulsin and the enzymes in yeast produce on the various glucosides prepared by synthetic methods, I was led to conclude not only that there was a difference between the two series of optical antipodes similar to that discovered by Pasteur in the course of his studies of moulds, but that very slight changes in configuration were sufficient to inhibit the action of enzymes entirely. I was led by these observations to apply the simile of *lock* and *key* as an expression of the close inter-relationship in configuration which obtains between the enzyme and the substance which it attacks.

Similar results were obtained on investigating the behaviour of the stereoisomeric hexoses with yeast, the fermentative power of which we now attribute to an enzyme: E. Buchner's zymase.

The experience gained with the glucosides became of service in studying the polysaccharides; for example, maltose and milk-sugar were found to differ in their behaviour towards the enzymes of yeast and emulsin much as do α- and β-methylglucoside. Another outcome of the investigation has been the discovery of distinct enzymes capable of attacking di- and tri-saccharides. Thus lactase was found to be present in Kefir grains and milk-sugar yeasts and definite proof was given of the presence of a maltase in beer yeast. As the result of these inquiries, I was able to formulate a rule of general biological significance, namely, that the alcoholic fermentation of a polysaccharide is necessarily preceded by its hydrolysis by some particular enzyme. It was shown, especially in the case of the invertase of *Monilia Candida*, that it is not essential that the enzyme should even be soluble in water. I may mention here that E. Buchner has himself admitted that he was led by these observations on *Monilia* to make his experiments on the mechanical separation of zymase from the yeast cell.

Unfortunately but few successful syntheses of polysaccharides have been effected. Musculus obtained dextrin-like products from grape-sugar by treating it with mineral acids; and I have shown that a disaccharide, *iso*maltose, may be produced in this way. E. Frankland Armstrong and I have prepared a number of disaccharides by synthesis from the acetylchlorohydroses; one of these products, probably, is identical with mellibiose.

But methods such as I refer to are so difficult in their application that their use cannot well be extended to any large number of polysaccharides. It is most desirable therefore that better methods should be devised, as it is probable that the attack on the dextrins, gums, and similar undeciphered substances is most likely to be successful if made from the synthetic side. It is to be expected that biology would gain much by the discovery and utilisation of such materials; more, perhaps, than it has from the study of the mono-saccharides and of the glucosides prepared by artificial means.

The carbohydrate group is that in which use was first made of enzymes as synthetic agents. You are aware that Croft Hill succeeded in preparing complex carbohydrates by subjecting glucose to the action of the enzymes in beer yeast. His contention that the product is maltose has been controverted; it is more probable that the condensation which glucose undergoes under the influence of the enzyme resembles that effected by hydrogen chloride, that is to say, that the product is a mixture of *iso*maltose with non-fermentable dextrins. In any case, Croft Hill has the great merit of having been the first to demonstrate the reversibility of enzyme action, and since his experiments were made similar results have been obtained with other enzymes, lipase, for example.

An important extension of Croft Hill's discovery is afforded by E. F. Armstrong's observation that the action of emulsin is different from that of the enzymes of yeast, the condensation of glucose taking place in such a way that a disaccharide which appears to be maltose is formed together with other complex products. Such syntheses effected by the agency of enzymes fascinate the imagination, as they approximate closely to natural processes; but I may point out that they cannot take the place of purely chemical methods, as these latter are so much more under our control, and can be varied in so many ways that we are in the position to produce materials which it is quite impossible for the organised world to furnish. Laboratory synthetic methods will be indispensable for a long time to come, not only for preparative purposes but also as the means of elucidating the structure of complex substances of natural origin.

This contention is applicable to the proteins even more than it is to the carbohydrates; as they are among the most complex substances produced in the living world, and are concerned in all the vital activities of the cell, a complete comprehension of their nature must obviously precede

the full development of biological chemistry. I may therefore be allowed to give very briefly a rapid survey of the present position of the chemistry of the proteins. The investigation necessarily began with the isolation and classification of the natural materials, and these were subdivided according to purely external characteristics, such as origin, solubility, coagulability, and the like. On the basis of such properties, we distinguish to-day some forty to fifty natural proteins, discovered by the joint labours of chemists and physiologists; but it is to be expected that as the methods of differentiating and separating them are improved, their number will be largely increased.

At present the majority are known only in an amorphous form; some important terms of the group, however, such as oxyhæmoglobin, egg albumin, and the albumin of horse serum, excelsin from the Brazil nut and the edestins from other plant seeds, have been obtained in definite crystals. But, unfortunately, it cannot be decided from their crystalline appearance whether these products are definite substances, as the tendency to form mixed crystals is the greater the more complicated the molecule. Examples in point are afforded by the aniline dyes, the higher fatty acids, and the purine compounds; and those who have studied the chemistry of the natural silicates will be aware of the extension which mineralogists have been compelled to give to the conception of isomorphism. It would therefore be altogether surprising if the crystallised natural proteins should turn out to be single substances. In this gathering of expert chemists I need not dwell on the difficulties to which this uncertainty gives rise.

(To be continued).

NOTICES OF BOOKS.

Practical Test Book of Chemistry. By JOHN DABNEY PALMER, M.A., M.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

THIS book contains an alphabetical arrangement of tests for the presence of various substances which the analytical chemist or pharmacist is likely to come across in the course of his work, and also tests for the purity of many foods and drugs. The methods have been collected from various sources, and have apparently not always been checked by the author himself, but have merely been copied from chemical and pharmaceutical journals. The various experiments appear to be described sufficiently fully as a rule, but in some cases a rearrangement of the order in which they are given would mean a possible saving of time for the experimenter, who will find no hints as to the relative sensitiveness or applicability of the tests. The examination of substances for purity is not well treated, and again the reader will look in vain for suggestions about the order in which he should apply the tests, so that he may in all cases search first for the most probable adulterants. As an instance of the author's method, we may call attention to the following case:—The analyst who had under his hand a sample of coffee for examination for purity would probably want to find quick and trustworthy methods of detecting the presence of common adulterants, and possibly estimating the amount of them present. When, however, he turned up "coffee" in the book he would find described only two experiments which would enable him to ascertain whether the sample contained any genuine coffee at all. Again, the methods given for examining butter are not sufficiently accurate or definite, and although they may be rapid and simple enough to show roughly whether the specimen examined contains large amounts of adulterant or not, they would probably be found quite inadequate to give any definite results in cases in which the adulteration had been skilfully carried out. The choice of substances in both parts of the book is purely arbitrary, and some omissions of important substances are by no means balanced by the details of the reactions of many rarer compounds which might possibly otherwise be found only by reference to original papers.

The Bacteriological Examination of Disinfectants. By WILLIAM PARTRIDGE, F.I.C. London: The Sanitary Publishing Company, Ltd. 1907.

THE greater part of this book is occupied with a complete description of the Rideal-Walker method of determining the germicidal value of a disinfectant. The author, owing to his familarity with the manipulation of the test, is in a position to give his readers many hints relating to details which may appear trivial, but which have, nevertheless, no little bearing upon the success of the method, and the neglect of which may lead to discrepancies. These small matters will receive the attention they deserve only from one who thoroughly realises that the bare outlines are not sufficient to enable the uninitiated to perform even comparatively simple tests in bacteriology, and they make all the difference to the practical usefulness of any book on the subject. The Preface is contributed by Major Fowler, R.A.M.C., who shortly discusses the question of the standardisation of disinfectants, and defends the Rideal-Walker method against those who criticise it owing to the apparently discrepant results which have been obtained when it is employed.

CORRESPONDENCE.

MELTING-POINTS.

To the Editor of the Chemical News.

SIR,—I shall be glad if any reader can inform me whether the melting-points are known of butane, pentane, and the higher members of the paraffin series up to octane, and, if so, where information on the subject can be found.

The melting-points of methane, ethane, and propane indicate that compounds containing an uneven number of carbon atoms are lower than those containing an even number, and it would be interesting to know whether this feature continues in the higher members of the series.—I am, &c.,

ED. E. PRICE.

MISCELLANEOUS.

Direct Quantitative Separation of Chlorides and Bromides.—A correspondent points out that the equation on p. 183, vol. xcvi., of the CHEMICAL NEWS, in Mr. Andrews's article on this subject, should be—

$$2KH(IO_3)_2 + 20KBr + 11H_2SO_4 = 10Br_2 + 2I_2 + 12H_2O + 11K_2SO_4.$$

MEETINGS FOR THE WEEK.

FRIDAY, 25th.—Physical, 5. "Use of Variable Mutual Inductances," by A. Campbell. "Magnetic Oscillators as Radiators in Wireless Telegraphy," by J. A. Fleming.

TUESDAY, 29th.—Faraday Society, 8. "Electrolysis of Salt Solutions in Liquefied Sulphur Dioxide at Low Temperatures," by B. D. Steele. "Action of Aluminium Powder on Silica and Boric Anhydride," by F. E. Weston and H. R. Ellis. "Reduction of Metallic Oxides by means of Calcium Hydride," by F. M. Perkin and L. Pratt. Exhibition of a Series-parallel Lamp Resistance useful for Electro-chemical Work, by N. T. M. Wilsmore.

THE CHEMICAL NEWS.

Vol. XCVI., No. 2501.

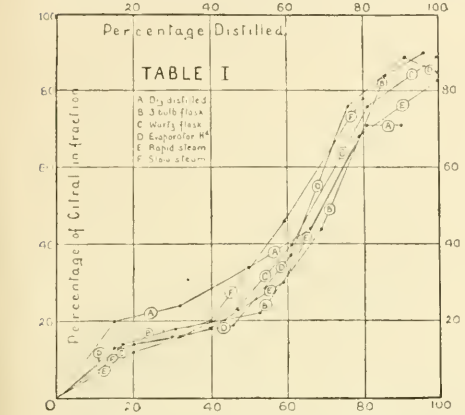
FRACTIONAL DISTILLATION BY MEANS OF STEAM.*

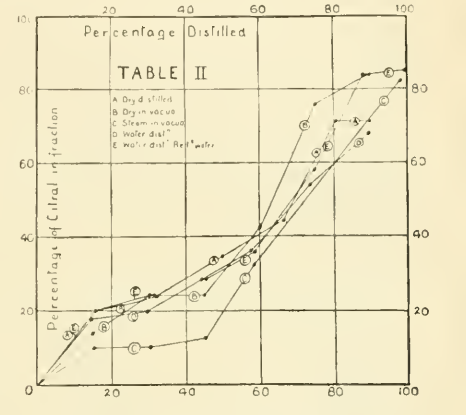
By HERBERT HARDY and BERNARD E. RICHENS.

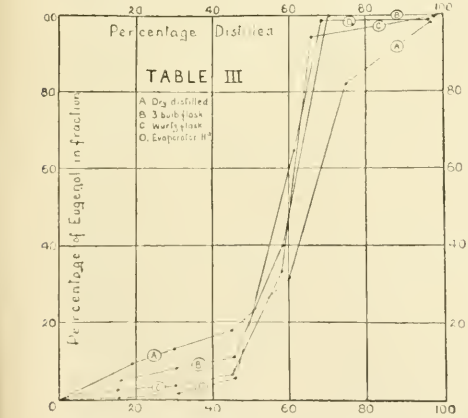
We have experimented in regard to the degree of fractionation that may be obtained when two liquids that are immiscible with water are distilled in a current of live steam; and, in the result, we find that if their boiling-points are not too close together, they may be separated as well—and often better—by steam distillation as by ordinary ("dry") distillation.

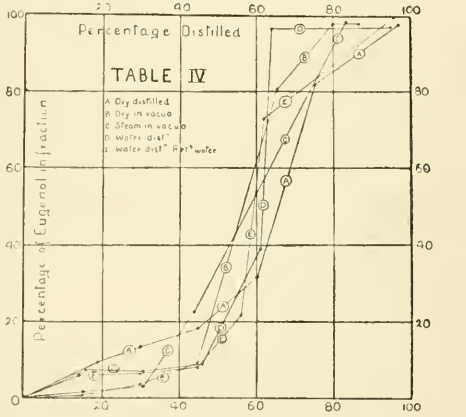
The accompanying tables apply to results obtained with mixtures of (*a*) limonene and citral (I. and II.) and (*b*) limonene and eugenol (III. and IV.) in equal volumes, and indicate the percentage of citral or eugenol in each fraction collected.

"Water distillation" means that the mixture of chemicals and water was distilled together from the same flask (in place of passing the steam from a separate boiler, as in the other cases), and "returning water" refers to a similar series of experiments where the aqueous portion of the distillate was returned to the distilling flask from time to time, so as to keep the volume of liquid in the flask nearly constant.









The "evaporator head" was a Young-Thomas modified evaporator head with three compartments.

The rate of distillation was normally 60 drops per minute of total distillate (water, &c.), but we also worked at 40 drops ("slow steam") and 180 drops ("rapid steam") per minute.

* Abstract of a Paper read before the Society of Public Analysts, December 5, 1906. The original appeared in the *Analyst* for June, 1907, and we are indebted to the Editor of that journal for the loan of the blocks illustrating th s article

As may be seen from the curves, the general results are —(*a*) That distillation by means of steam gives *at least* as good a fractionation as ordinary dry distillation; (*b*) that steam under reduced pressure is specially efficient; (*c*) that the use of a fractionating column has but little effect; and (*d*) that the results are but slightly influenced by the rate of distillation, the more rapid being rather better.

The method applies only to substances insoluble in water.

Limonene and cineol have both b. p. 176° C. and citral 228—230°.

RED SEA WATER.

By JOHN B. COPPOCK, B.Sc. (Lond.), F.I.C., F.C.S.

DURING September of this year a sample of Red Sea water, from Port Soudan, came into my hands for analysis. No analysis of this sea water seems to have been recorded, hence it was thought desirable to publish the following figures.

The analysis is of the usual type as far as the inorganic constituents of sea-water are concerned, but differs from the usual type by the determination of the constituents usually in water analysis grouped under the heading "free and albumenoid ammonia." These latter substances were determined by a modification of the American official alkaline permanganate method for nitrogen availability in tankage, sodium nitrate, &c., and which has been shown to give satisfactory results.

Analytical Figures.

	Per cent.
Total solids—	
Amount obtained by evaporation at 100° C..	4·84
Amount obtained when dried in steam-oven and finished in desiccator	4·34
Inorganic substances—	
Chlorine	2·09
Sodium	1·18
Magnesium	0·135
Calcium	0·052
Sulphates (SO_4)	0·206
Carbonates (CO_3)	0·007
	3·670
Other constituents and water of crystallisation	1·170
	4·840
Ammonia determinations—	
Free ammonia	0·00014
Calculated as NH_4Cl	0·00043
Albumenoid ammonia	0·00042
Calculated as albumenoids	0·00222

The free ammonia represents that which came off on distillation with a small quantity of sodium carbonate; the albumenoid ammonia that which came off on treatment of the water with 15 grms. of caustic soda and 1·6 grms. of potassium permanganate.

Specific gravity at 10° C., 1·027.

Chemical Laboratory, Kendal.

Action of Alkalis on Tetrathionates.—A. Gutmann. —When about 15 per cent alkali solution, NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$, acts upon a tetrathionate sulphite and thiosulphate are formed: $2S_4O_5 = 3S_2O_2 + 2SO_2$ or $2S_4O_6Na_2 + 6NaOH = 3S_2O_3Na_2 + 2SO_3Na_2 + 3H_2O$. If concentrated alkali solution (1 : 1) is used some sulphide is obtained in addition, the reaction being $3S_4O_5 + H_2O = 3S_2O_2 + 5SO_2 + H_2S$ or $3S_4O_6Na_2 + 12NaOH = 3S_2O_3Na_2 + 5SO_3Na_2 + Na_2S + 6H_2O$. No sulphate was formed in the author's experiments.—*Berichte*, xl., No. 13.

SYNTHETICAL CHEMISTRY IN ITS RELATION TO BIOLOGY.*

By Prof. EMIL FISCHER, F.R.S.

(Concluded from p. 210).

OF the numerous attempts to unravel the constitution of the proteins by analytical means, the only method which has given useful results hitherto is that of hydrolysis. Hydrolysis can be effected by acids or by alkalis, and also by digestive enzymes; the products, it is well known, besides ammonia, are albumoses, peptones, and ultimately amino-acids. The wide range of variation in composition of these amino-acids is illustrated in the following list:—

Glycine (Braconnot, 1820).
Alanine (Schützenberger, Weyl, 1888).
Valine (v. Gorup-Besanez, 1856).
Leucine (Proust, 1818; Braconnot, 1820).
*iso*Leucine (F. Ehrlich, 1903).
Phenylalanine (E. Schulze and Barbieri, 1881).
Serine (Cramer, 1865).
Tyrosine (Liebig, 1846).
Aspartic acid (Plisson, 1827).
Glutamic acid (Ritthausen, 1866).
Proline (E. Fischer, 1901).
Oxyproline (E. Fischer, 1902).
Ornithine (M. Jaffé, 1877).
Lysine (E. Drechsel, 1889).
Arginine (E. Schulz and E. Steiger, 1886).
Histidine (A. Kossel, 1896).
Tryptophane (Hopkins and Cole, 1901).
Diaminotrihydroxydodecanoic acid (E. Fischer and E. Abderhalden, Skraup, 1904).
Cystine (Wollaston, 1810; K. A. H. Mörner, 1899).

In this list are included all the substances hitherto prepared from the proteins the existence of which is established, with a short reference to their discovery. It may, however, be mentioned that the list is by no means complete; among the new products already announced, the caseanic acid described by Skraup appears to have the greatest claim to recognition as a definite substance. It is certain, however, that the nineteen amino-acids in the list are the chief hydrolytic cleavage products of the proteins and those which are most generally met with. Their discovery has been made during a period of eighty-four years, but no less than five of them have been recognised within the new century.

The proportions in which the various amino-acids are obtained from the different proteins vary very considerably. In some cases they are altogether lacking, as may be proved by application of the definite tests for tyrosine, tryptophane, or glycine; but it is worthy of note that, as a rule, the amino-acids referred to as isolated from the mixtures produced by subjecting albuminous substances to hydrolysis all occur almost without exception, especially is this true of the important proteins which play the chief part in animal or vegetable metabolism, so that the conclusion must be drawn that none of them can be dispensed with in organic life. With the exception of diaminotrihydroxydodecanoic acid, they have all been so thoroughly investigated that their structure is well established. The majority also have been synthesised, proof of their structure having, in fact, been given in this way. Only oxyproline, histidine, and diaminotrihydroxydodecanoic acid remain still to be synthesised.

With the exception of glycine, all the amino-acids derived from natural sources are optically active; but when prepared by ordinary synthetic methods, as is well known, they are obtained in the first instance in the racemic form. The resolution of the racemoids into their optically active

* Faraday Lecture, delivered before the Chemical Society, October 18, 1907. From the *Transactions of the Chemical Society*, 1907, vol. xci.

components has been effected quite recently in most cases. Asparagine, however, which is closely related to aspartic acid, has been resolved into the two active forms by recrystallising the inactive synthetic product from water, and separating the two constituents mechanically. Moreover, in the case of some other amino-acids, for example, leucine, the antipode of the natural form had been obtained by partially fermenting the synthetic product with moulds. The complete synthesis of the active amino-acids which are obtained from natural sources was first accomplished by the method I introduced based upon the use of the acyl derivatives. The method has been applied with success to the majority of the synthetic products; its extension to the remaining cases, proline, lysine, tryptophane, and cystine, is not likely to be attended with any difficulties. The synthetical results are summarised in the following list, in which the inactive products are marked *dl* and the natural active products are recorded separately:—

Glycine (Perkin and Duppa, 1858).
Alanine *dl*- (A. Strecker, 1850).
Alanine *d*- (E. Fischer, 1899).
Valine *dl*- (Fittig and Clark, 1866).
Valine *d*- (Fischer, 1906).
Leucine *dl*- (Limpricht, 1855; E. Schulze and Likiernik, 1885).
Leucine *l*- (Fischer, 1900).
*iso*Leucine *dl*- (Bouveault and Loquin, 1905).
*iso*Leucine *d*- (Loquin, 1907).
Phenylalanine *dl*- (Erlenmeyer and Lipp, 1883).
Phenylalanine *l*- (Fischer and Schöller, 1907).
Serine *dl*- (Fischer and Leuchs, 1902).
Serine *l*- (Fischer and Jacobs, 1906).
Tyrosine *dl*- (Erlenmeyer and Lipp, 1883).
Tyrosine *l*- (Fischer, 1900)
Aspartic acid *dl*- (Dessaignes, 1850).
Aspartic acid *l*- (Piutti, 1887).
Glutamic acid *dl* (L. Wolff, 1890).
Glutamic acid *d*- (Fischer, 1899).
Proline *dl*- (R. Willstätter, 1900).
Ornithine *dl*- (Fischer, 1900).
Ornithine *d*- (Sörensen, 1905).
Arginine, active; partial synthesis from ornithine (E. Schulze and Winterstein, 1899).
Lysine *dl*- (Fischer and Weigert, 1902).
Tryptophane *dl*- (A. Ellinger and Flamand, 1907).
Cystine *dl*- (Erlenmeyer, jun., 1903).

I have been able to refer the configuration of some of these substances to that of glucose. This correlation was first effected thirteen years ago in the case of aspartic acid. As you are aware, this acid is converted by nitrous acid into *l*-malic acid, the configuration of which can be deduced from its relationship to tartaric acid. In a similar manner, it has been found possible recently to connect serine and alanine with active glyceric acid, which Neuberg and Silbermann have been able to correlate with tartaric acid, and which it may be anticipated will also be obtained directly from the tetroses by adopting methods such as those introduced by Wohl and Ruff. It will probably be found that the method is applicable to most of the other amino-acids, so that it is to be expected that at no distant date a uniform steric system will be established which will include all the optically active substances in the sugar group, the hydroxy-acids, and the amino-acids.

It is not without purpose that I have dwelt so long on what appear to be side issues of synthetic work, for I firmly believe that they will prove in many respects to be of service to biological inquiry. In proof of this, reference may be made to several cases in which they have already borne fruit. For example, the proof given by E. Schulze and Winterstein that arginine is a derivative of guanidine, and therefore also of urea, had undoubtedly some influence in stimulating H. Kossel to the discovery of the interesting manner in which this amino-acid is resolved into urea and ornithine by means of liver arginase.

To test the assumption that ornithine and lysine are carboxylic acids of tetra- and penta-methylenediamines, Ellinger subjected these substances to the action of putrefactive bacteria, and was successful in converting them into the well-known basic products of putrefaction.

The manner in which taurine is formed in the animal body has been made clear by Friedmann's proof of the relation between cystine and taurine.

The isolation of tryptophane by Hopkins and Cole, and its conversion into scatole, enable us to form a clear picture of the manner in which this offensive substance is produced by intestinal putrefaction, and to indicate also the origin of the indoxylsulphuric acid discovered by E. Baumann in urine, and of the indigo-blue which is sometimes met with in this secretion. I need do no more than point out, however, that this connection could not possibly have been established had not A. von Baeyer laid the foundation by his great synthetic achievements in the indigo group.

The discovery of *iso*leucine and its relationship to leucine led F. Ehrlich, a few years ago, to undertake his interesting experiments on the conversion of amino-acids into primary alcohols by means of beer yeast, which enabled him to give the long-sought explanation of the formation of fusel oil during alcoholic fermentation.

Such instances will be multiplied rapidly in the future; considerations of the relationship of the natural amino-acids to various other classes of substance from the structural and stereo-chemical point of view are formulated so easily and in such a variety of directions that they can afford much fruitful stimulus to physiological inquiry.

As the amino-acids are formed from the proteins, not only when these are subjected to the action of hot acids and alkalis but also at moderate temperatures by the agency of the digestive enzymes, they are to be regarded as the true foundation stones of protein molecules. Opinions adverse to this hypothesis are only occasionally met with; they centre round the arbitrary supposition that complicated atomic re-arrangements may take place during hydrolysis.

Were one inclined to regard such objections as of moment, all the experiments on the determination of the constitution of organic compounds by degradation methods would be useless; moreover, the conclusions which have been drawn in other cases from the results obtained by the dissection of compounds have been too frequently confirmed by their synthesis. It is now possible to make this claim on behalf of the proteins, as it has been found to be possible, by a process the reverse of hydrolysis, to associate amino-acids in such a manner that substances are produced which, in the case of the simpler terms, closely resemble peptones, whilst the more complex resemble proteins.

I have termed these synthetic products *polypeptides*, in view of their relationship to the peptones and to facilitate systematic treatment of the group on the lines of the carbohydrates.

No useful purpose will be served by my giving an account of the synthetical methods on the present occasion, especially as I had the honour, six months ago, of describing to you the preparation of an octadecapeptide derived from 15 molecules of glycine and 3 molecules of *l*-leucine, a substance which in its external properties closely resembles many natural proteins. I may say that more than one hundred of these artificial polypeptides have already been synthesised.

Many of them, it is true, belong to the lower stages, but all the amino-acids previously mentioned, with the exception of diaminotrihydroxydodecanoic acid, have been made use of in their preparation. The synthesis of the higher terms has been restricted hitherto to the combinations of glycine, alanine, and leucine; there is not a shadow of doubt, however, that all the remaining amino-acids could be associated in complicated systems with the aid of our present methods. The knowledge of the artificial polypeptides thus acquired has opened up new ways of investigating the peptones and albumoses analytically. During

more than fifty years, physiological chemists have endeavoured without much success to isolate homogeneous substances from these ill-defined materials; all the products described by them, however, bear indubitable evidence of being mixtures. By making use of new methods based on the study of the polypeptides, it has been possible during the last two years to isolate and detect with certainty quite a number of dipeptides among the decomposition products of the proteins. In conjunction with Abderhalden, I have succeeded in separating glycyl-*d*-alanine, *d*-alanyl-*l*-leucine, and *l*-leucyl-*d* glutamic acid from silk fibroin, elastin, and gliadin respectively. We have definitely proved the existence of dipeptides of glycine with *l*-leucine and *l*-tyrosine in the form of anhydrides, and our work has made it probable that other combinations exist; for example, that of glycine with valine. P. A. Levene has discovered glycyl-proline anhydride among the products of the digestion of gelatin, whilst T. B. Osborne and S. H. Clapp have noted a dipeptide derived from phenyl-alanine and proline among the products of the hydrolysis of gliadin by hot sulphuric acid. A tetrapeptide of fairly definite composition has been isolated by Abderhalden and myself from silk fibroin, and, although its homogeneity is not yet quite established, it is certainly in great part a combination derived from two glycine molecules with one of *d*-alanine and one of *l*-tyrosine. The substance is of special interest on account of its close resemblance to the albumoses. Moreover, *l*-leucyl-triglycyl-*l*-tyrosine prepared artificially has all the properties of the albumoses. These observations are of importance as casting doubt on the view which formerly prevailed that, being intermediate products between proteins and peptones, the albumoses are substances of considerable molecular complexity.

This may be true of many of the substances hitherto described under the name, all of which are certainly mixtures; but it is clear that many others are no more complex than the albumose above referred to from silk or the artificial pentapeptide.

In spite of these encouraging successes, I am fully aware of the difficulty of discovering the nature of all the components of the various peptones and albumoses. But in preparing the way for the synthesis of the natural proteins this is not even necessary. Probably the work can be restricted to the re-construction of the original system from the major products of cleavage formed in the process of hydrolytic dissection. I am, indeed, venturesome enough to cherish the hope that I may be able to solve this problem in the case of silk fibroin, one of the simplest proteins. To deal with the whole of the proteins will be a gigantic task; so large a number of separate investigations will be necessary that nothing less than the life-work of a whole army of inventive and diligent chemists will suffice to complete it. Probably, too, the unpleasant discovery will be made that the natural proteins as we know them to-day are only to be obtained by mixing the homogeneous artificial products.

I have sketched this prospect merely to indicate the manner in which synthesis must play the leading part in this field of work. The nature of the more complicated carbohydrates, as I have already pointed out, will also have to be determined in the future, I imagine, mainly by the application of synthetic methods. Obviously the conditions are very similar in the case of the dextrins and gums to those met with in the case of the proteins, and starch, which has hitherto been regarded as a homogeneous substance, appears also to come into the same category, according to Maquenne's observations.

Not only do the proteins constitute the major part of living protoplasm, but they appear also to be the material from which the organism prepares its most wonderful agents; the ferments or enzymes. In many of the more thoroughly investigated biological processes their co-operation has been demonstrated, and there is good reason to suppose that they take part in all changes occurring within the living cell. So much is certain, the physiological chemistry of the future will be largely concerned with the study of fermentative changes; many indications that this must be the case are to be met with in tracing its latest developments.

The number of the enzymes has been increased to an extraordinary extent during the last ten years. I may allude to the newly-discovered enzymes correlated with the carbohydrates, maltase, lactase, mellibase, trehalase, amygdalase, inulase; to the various oxidases, laccase, tyrosinase; to the lipases, erepsin, enterokinase, arginase, the sucroclastic and glucosidoclastic enzymes, and finally to the zymase of alcoholic fermentation. Much valuable information has been accumulated as to the manner in which they act, as to their formation from zymogens, and as to their assistance by co-ferments and their retardation by chemical agents or by antiferments. The specific character of their action, in other words, their dependence on the structure and configuration of the object they attack, has been proved beyond doubt, and favours very definitely the assumption that enzyme and hydrolyte enter temporarily into combination, a conclusion to which H. E. Armstrong and E. F. Armstrong have quite recently again very properly drawn special attention. But, unfortunately, we know practically nothing of the composition of the enzymes, as the complete isolation of an enzyme has never been accomplished.

From observations hitherto made, it appears in a measure probable that they are derived from proteins, and possess a protein-like character. If this be so, it may be hoped that the experience gained with the proteins will be of service in the investigation of enzymes.

In the meantime there are other directions in which synthetic chemistry can be of service in elucidating the chemistry of fermentation. In the same way that the artificial glucosides have been of use in establishing the dependence of the action of enzymes on configuration, the synthesised polypeptides are now being used by Abderhalden, Euler, and others to define and measure the activity of the proteoclasts. In a like manner, the synthetic exploration of the purine group has served to direct the recent observations on the fermentative de-amination and oxidation of adenine, guanine, and xanthine. Finally, attention may be directed to the use that has been made of stereochemical considerations in the course of Bertrand's interesting studies of the oxidation of polyhydric alcohols by the sorbose bacterium.

Not only have the methods of organic chemistry proved to be fruitful of results in the case of the proteins but also when applied to complex derivatives of the latter, such as the nucleo-proteins, for example. Thus we are indebted to the brilliant researches of A. Kossel and his school for our knowledge of no less than four bases of the pyrimide and purine group obtained by breaking down nucleic acids, and the analytical investigation of the latter has already been carried so far that, in the opinion of H. Steudel, it is to be expected that their synthesis will be effected at no distant date. Similar success may be hoped for even sooner in the case of the lecithins. Structural chemistry, moreover, is slowly acquiring the mastery over cholesterin by making use of the experience afforded by the synthetic study of the hydroaromatic substances.

Besides the old well-known constituents of the animal body, new substances having quite unexpected properties have been added from time to time. Such are iodothyrin from the thyroid gland—discovered by Baumann—and crystalline adrenaline—isolated by Takamine from the supra-renal capsule—minute doses of which increase the blood-pressure. Judging from analytical results and the synthesis effected by F. Stolz, adrenaline possesses a relatively simple structure. In the opinion of the discoverers, this is probably true of the "pancreatic secretin" made known by Bayliss and Starling's researches, which has the remarkable property of liberating enzymes from the pancreas. May it not also be true of the toxins of many infectious diseases and of the antitoxins used in serum therapeutics, the discovery and systematic investigation of

which by Behring, Roux, P. Ehrlich, and others are to be reckoned among the greatest achievements of modern biology and medicine?

The methods of organic synthesis will certainly serve to throw light on the nature of all such substances of animal origin. Equally numerous problems await solution in the plant world.

The great success with which the alkaloids and terpenes have been studied during the past ten years is known to all, but it is only too obvious that much still remains to be done when such substances as quinine, morphine, and caoutchouc remain to be synthesised.

Alizarin and indigo are prepared artificially in huge quantities, and we are well informed as to the structure of hæmatoxylin and kindred substances; but our ignorance is correspondingly great of most of the blood colouring matters as well as of many coloured constituents of our own bodies: of the air, the skin, and the eye.

The fullest recognition must be accorded, however, to recent investigations on the complex colouring matters of the blood and of chlorophyll, which is distantly related to the former, associated with the names of Schunck, Nencki, Marchlewski, Küster, and Willstätter.

In fine, the aid of synthetical chemistry is required in every direction in arriving at a clear understanding of structure and of change. The methods at our disposal in the laboratory are doubtless altogether different from those which come into operation in the living world, but chemists are already trying to effect changes in carbon compounds by means of so-called mild interactions, under conditions comparable with those which prevail in the living organism. It may suffice to refer to the development of a number of catalytic processes, and to the comprehensive studies on the action of light on organic substances undertaken by Ciamician. In fact, the effort is already being made to co-operate with biology; it is clear that a section of the forces of organic chemistry are being directed once more towards the goal from which it set out. The separation from biology was necessary during the past century while experimental methods and theories were being elaborated; now that our science is provided with a powerful armoury of analytical and synthetical weapons, chemists can once more renew the alliance both to its own honour and to the advantage of biology. Indeed, the prospect of obtaining a clearer insight into the wondrous series of processes which constitute animal and vegetable life may well lead the two sciences to work with definite purpose to a common end.

In order, as far as possible, to avoid mistakes in this difficult task, and to shield ourselves from the disappointment which is the inevitable consequence of exaggerated hopes, we cannot do better than strive to imitate the great example of Faraday, who always with rare acumen, directed his attention to actual phenomena without allowing himself to be influenced by preconceived opinion, and who in his theoretical conceptions gave expression only to observed facts.

Dennstedt's Simplified Combustion Method.—R. Baumert.—The author finds that in Dennstedt's method substances which generate gases which burn with difficulty often fail to undergo complete combustion. The following modification of the method is rather simpler and more satisfactory. The same furnace is used, but the tubes have the ordinary combustion tubing diameter of 18 mm., and the boats, &c., are smaller in proportion. Instead of platinum quartz copper oxide asbestos is used for substances which do not contain halogens and platinum asbestos for those which do. Silver asbestos is used instead of molecular silver, and lead peroxide asbestos instead of lead peroxide. The absorption apparatus is the same as Prof. Dennstedt's.—*Berichte*, 1907, xl., No. 13.

THE MOLECULAR WEIGHT OF ARGENTIC SULPHATE.

AND THE ATOMIC WEIGHT OF SULPHUR.*

By THEODORE WM. RICHARDS and GRINNELL JONES.

(Concluded from p. 205).

The Conversion of Argentic Sulphate into Chloride.

The next step in the process was the conversion of the carefully weighed fused sulphate into chloride by heating it in a current of dry hydrochloric acid gas. This reaction has been observed by Hensgen (*Recueil des Travaux Chimiques de Pays-Bas.*, 1883, ii., 121):—

"Le sulfate d'argent absorba 2 mol. HCl à la température ordinaire, avec un dégagement de chaleur notable, et se changea complètement en chlorure. En chauffant, même jusqu'a 300°, la réaction inverse (observée par M. H. avec le sulfate de cuivre) n'eut point lieu, mais l'acide sulphurique fut chassé complètement par un courant d'air. Parmi les sels susdits, le sulfate d'argent est celui qui d'après les données thermiques doit se changer en chlorure avec le plus grand dégagement de chaleur." (See below).

The hydrochloric acid generator used for the previous work was constructed entirely out of glass. Pure ammonic chloride or concentrated hydrochloric acid was placed in the flask (I) shown in Fig. 2, and concentrated sulphuric acid was dropped upon it slowly. The gas was dried by passing through the tower (J) containing beads moistened with concentrated sulphuric acid (see Note). The gas then passed through the stopcock (K) to the delivery tube (N). The ground-glass stopper at the top of the tower (J) acted as a safety-valve when the stopcock (K) was closed. Pure dry air might also be delivered at N by means of the stopcock (L), in order to sweep out the excess of acid at the conclusion of the reaction.

(Note.—In one of the preliminary experiments the hydrochloric acid was not dried. The sulphuric acid first formed absorbed considerable water, thus becoming diluted and nearly filling the tube with liquid sulphuric acid in which a large part of the silver sulphate dissolved. After heating for some time, the whole mass was solidified. This gave a non-porous mixture of silver sulphate and chloride. The hydrochloric acid had no appreciable further action until the mixture was fused, and then the action became very vigorous. The sulphuric acid which was formed boiled, and caused spattering, and therefore danger of mechanical loss).

The quartz tube containing the argentic sulphate was supported by means of hooks of hard glass in front of the delivery tube (N), as before, without making a tight joint.

In seven of the final experiments a condenser tube of quartz (O) was placed over the exit end of the tube (M) in order to condense the sulphuric acid and retain any silver which might escape. As will be shown, only very small traces of silver were found in the distillate. The condensation of sulphuric acid in the narrow tubes on the end was prevented by keeping them hot by means of a small fixed fish-tail burner.

A slow current of hydrochloric acid was generated, and the tube warmed gently. The reaction took place readily and quietly, the only difficulty being that the argentic chloride formed was inclined to creep over the walls of the vessel. This was probably due to the liberated sulphuric acid having dissolved undecomposed argentic sulphate; the acid sulphate was then transported by surface tension, and converted into chloride in another place. In two of the experiments one of the narrow end tubes was completely blocked up in this manner, making a successful completion of the experiment impossible, but in other cases the difficulty was avoided by starting with the argentic sulphate in a band in the middle of the tube.

The sulphuric acid must be evaporated at a temperature below its boiling-point in order to avoid loss by the pro-

* *Publication* No. 69, Carnegie Institution of Washington.

jection of small particles. The tube was heated by a flame held in the hand, the heating being regulated by watching the escaping fumes of acid and also the colour of the argentic chloride in the tube. It is well known that as the temperature increases, silver chloride acquires a deeper and deeper yellow colour, and after acquiring the necessary experience, this change of colour proved very helpful in egulating the temperature.

After from 2·5 to four hours no more fumes of sulphuric acid could be seen issuing from the tube. The argentic chloride was then fused very slowly and quietly, and kept in the fused state for twenty minutes in a current of hydrochloric acid. The tube was gently agitated in order to expose a fresh surface, at intervals of about one minute, by grasping the exit end with platinum forceps. The agitation can be performed without danger of loss, because of the high surface tension of fused argentic chloride. This material when liquefied does not adhere to quartz, and therefore is not drawn into the end tubes by capillarity. At the expiration of twenty minutes the current of acid gas was stopped by means of the stopcock (K), and a current of pure dry air was passed through the tube through L, the argentic chloride being still maintained in the liquid state for at least five minutes with occasional agitation. The tube was rotated while subsequently cooling in a similar manner to that employed with the sulphate.

The condensed sulphuric acid evolved by the reaction and the condenser tube were tested for silver by means of the nephelometer (Richards and Wells, *Am. Chem. Journ.*, 1904, xxxi., 235). The acid was transferred to a small flask, and the tube was rinsed with ammonia, which was added to the acid. The excess of ammonia was then neutralised with nitric acid, and hydrochloric acid was added to precipitate any trace of silver present as an opalescent cloud of argentic chloride. This opalescence was compared in the nephelometer with a standard which had been made in a manner very similar to the unknown solution (Richards, *Am. Chem. Journ.*, 1906, xxxv., 510). A measured volume of a standard silver solution was taken; to it were added approximately the same amounts of sulphuric acid, ammonia, and nitric and hydrochloric acids as were present in the unknown solution, and it was made up to the same volume (about 30 millilitres).

The greatest amount of argentic chloride thus found in any experiment was 0·00009 grm., and the average amount 0·00004 grm. The trace found in this way was of course added to the weight of the silver chloride. In three of the experiments (Nos. 4, 5, and 7) this determination was not made, but the average amount is added in these cases. The probable reason for the escape of this trace of silver will be discussed later.

The question as to whether or not this reaction is complete is, of course, of fundamental importance. There are four pieces of evidence bearing on this point.

In the first place, the argentic chloride was fused for twenty minutes in a current of almost pure hydrochloric acid. Since the temperature was far above the boiling-point of sulphuric acid, this product of the reaction was driven off as fast as formed. Therefore, according to the law of concentration-effect it is to be expected that, through the agency of the continually renewed hydrochloric acid, all the argentic sulphate would be decomposed, and all the sulphuric acid would be driven off. This would be hastened by the fact that fresh surfaces were continually exposed through agitation.

Again, in this case the law of concentration-effect is assisted by the relative affinity, indicated approximately by the large amount of heat evolved by the reaction. It can be calculated from Thomsen's data that the reaction gives out 40,400 grm.-calories, or 170 kilojoules (see Note). Rarely, if ever, is the difference between total-energy and free-energy changes in a reaction of this kind as great as this, hence it is safe to infer that there is a considerable preponderance of driving tendency in the desired direction, arising from the mutual affinities concerned.

NOTE. — Thomsen, "Thermochemische Untersuchungen":—

$2Ag + Cl_2 = 2AgCl + 58760$ (vol. iii., p. 381).

$Ag_2SO_4 = 2Ag + O_2 + SO_2 - 96200$ (vol. iii., p. 382).

$SO_2 + O_2 + H_2 = H_2SO_4 + 121840$ (vol. ii., p. 255).

$2HCl = H_2 + Cl_2 - 44000$ (vol. ii., p. 114).

Therefore, $Ag_2SO_4 + 2HCl$ (gaseous) $= 2AgCl + H_2SO_4$ (liquid) $+ 40400$.

A different set of equations gave 40,200. The result, of course, only applies to 18°. In this connection it is worth while to note that $Ag_2SO_4 + Cl_2 = 2AgCl + SO_2 + O_2 - 37440$ cals.; which indicates that chlorine would not be as suitable for our purpose as hydrochloric acid. This expectation is confirmed by the experience of Krutwig (*Ber.*, 1881, xiv., 306): —"Die Einwirkung ist hier (chlorine on silver sulphate) keine direkte; nur bei sehr hoher Temperatur, nachdem das Salz geschmolzen ist und sich zersetz, giebt es schweflige Saüre, Chlorsilber, und Sauerstoff ab."

Thirdly, constancy of the weight on continued treatment indicated the completion of the reaction. In seven of the experiments the argentic chloride was fused a second time in hydrochloric acid for fifteen minutes with occasional agitation, followed by five minutes in air. The following table gives the changes in weight found in this way:—

The Effect of Continued Treatment with Hydrochloric Acid.

No. of experiment	AgCl, first weighing.	AgCl, second weighing.	Difference.
6.	4·67812	4·67809	−0·00003
7.	4·93119	4·93118	−0·00001
11.	4·67373	4·67375	+0·00002
13.	4·74491	4·74489	−0·00002
14.	4·77995	4·77990	−0·00005
15.	4·94088	4·94088	0·00000
		Average	−0·000015

The constancy in weight was thus entirely satisfactory, the average loss being only 0·0003 per cent of the weight of the chloride.

This experiment, however, does not absolutely preclude the possibility that a small but constant amount of sulphate may remain. In order to test this question, 4·90 grms. of argentic chloride which had never been contaminated with sulphate was fused in the tube, and then 0·00479 grm. of pure argentic sulphate was added and thoroughly mixed with the chloride by fusion. On cooling, the appearance was very different from the pure chloride, the mass being translucent or almost opaque instead of transparent. It was then fused in a current of hydrochloric acid for twenty minutes after the sulphuric acid could no longer be seen escaping from the tube, as before. On the assumption that the sulphate was converted completely into chloride the loss in weight would have been 0·00039 grm., while the actual loss in weight was 0·00044 grm. The reaction was evidently complete, and a fourth argument was added to the other reasons for believing that the process should yield satisfactory results.

It will be recalled that the narrow end tubes were kept very hot by small stationary burners in order to prevent the condensation of sulphuric acid. At the close of several of the experiments a very slight sublimate was observed on the portion of the narrow tubes which was kept somewhat cooler by the protection of the supporting hooks. This sublimate, although never large in amount, appeared largest in Experiments 6 and 10. There was a smaller amount in Experiments 7, 11, and 14, but none worthy of consideration in Experiments 4, 5, 12, 13, and 15. In Experiments 10 and 14 a slight amount of the sublimate was visible in the condenser also, near the end of the tube.

Although the most rational explanation of this trace of sublimate, which was usually too slight to be weighable, was probably to be found in the assumption that it was argentic chloride, and therefore entirely without sinister meaning except as suggesting the risk of the loss of other traces, the matter was studied further. Careful tests for

arsenic and copper were made with negative results, and the hydrochloric acid was demonstrated to contain no trace of anything which could be deposited in a red-hot quartz tube. (The test for arsenic was kindly made by Mr. O. F. Black). On the other hand, the sublimate was soluble in ammonia, and behaved in every way like argentic chloride, so that its nature was considered as nearly proved as was possible with such a minute amount of material. Having settled the nature of the sublimate, its source and significance must be traced. Evidently it could not have come from the main body of the silver sulphate, because it appeared at the very beginning of the experiment, as soon as the current of hydrochloric acid was started and the end tubes heated, before the heat was applied to the main body of the argentic sulphate. Moreover, the mass of the argentic chloride was never heated to a temperature high enough to volatilise weighable amounts of this substance, as was shown by the constancy of weight on continued heating in a current of gas. (See the preceding description; also Richards and Wells, *loc. cit.*, p. 60; Baxter, *Proc. Amer. Acad.*, 1905, xli., 83).

In view of these considerations, it seemed probable that a few invisible crystals of argentic sulphate had been left in the end tubes by the feather used in cleaning it, or carried into the end tube by the current of sulphur trioxide before fusion. As soon as the hydrochloric acid was admitted and the end tubes heated, these small invisible crystals of silver sulphate must have been at once converted into chloride, and sublimed to the cooler portion of the tube—for the end tubes were usually raised to a red heat. This explanation is consistent with the frequent absence of any significant sublimate, especially in the case of Experiment 15. In this experiment the tube had been dusted and treated with particular care, in order to test the point.

Because the sublimate was weighed in the tube which had previously contained the sulphate, its presence could not affect the accuracy of the results, even if it had been weighable. Nevertheless, the suggestion that another portion might have been carried out of the tube was worth considering. Doubts on this point were set at rest by the analysis of the contents of the condenser tube which received the volatile products of the reaction. The average amount of silver found in this tube was less than 0·001 per cent of that taken in each experiment, and the small appropriate correction was easily applied.

Although it was not probable that argentic chloride which had been fused in air for five minutes still retained any dissolved hydrochloric acid, this point also was tested. In Experiment 13, the silver chloride after the first heating in hydrochloric acid and fusion in air for five minutes as usual, weighed 4·74491 grms. After the second fusion in hydrochloric acid, and finally in air, the weight was 4·74489 grms. After another fusion for twenty minutes in a current of pure air, the weight was 4·74493 grms. These slight changes in weight can only be ascribed to errors in the weighing; the outcome shows that the argentic chloride after the usual treatment did not retain any dissolved hydrochloric acid. Richards and Wells (*loc. cit.*) have already shown that it does not dissolve weighable amounts of air.

In still another case the outside of the tube was washed with water to make sure that nothing had deposited on it during the long exposure to the flame and acid. The loss in weight was only 0·02 mgrm., which again is not greater than the possible error in weighing.

The Final Results.

Having shown the feasibility of the plan of operations and gained practice by three preliminary experiments, a final series was undertaken, whose outcome is detailed below.

Sample A of argentic sulphate was used in Experiments 4 and 5, and Sample B in the remainder. In Experiments 5 and 6 the hydrochloric acid was generated from ammonic chloride, and in the other experiments from concentrated hydrochloric acid. The corrected weight of argentic chloride was obtained by adding the trace found in the condenser to the average weight after fusion in hydrochloric acid. In Experiments 4, 5, and 7 the correction for the argentic chloride in the condenser was not determined directly, but the mean of the other determinations (0·00004 grm.) was added.

In Experiments 8 and 9 the narrow exit tube became completely blocked by the creeping of the argentic chloride. This made it necessary to fuse the solid while there was still present considerable argentic sulphate; and therefore the sulphuric acid boiled and material was lost by being projected out of the tube. The first of these was rejected and the second not finished. All the other determinations are recorded in full in the table. The weighings have of course been corrected to the vacuum standard.

The Quantitative Conversion of Argentic Sulphate to Chloride.

No. of experiment.	Weight of colourless Ag_2SO_4 in vacuum.	Weight of total AgCl in vacuum.	Parts of AgCl obtained from 100·000 parts of Ag_2SO_4.
4.	5·21962	4·79859	91·934
5.	5·27924	4·85330	91·932
6.	5·08853	4·67810	91·934
7.	5·36381	4·93118	91·934
10.	5·16313	4·74668	91·934
11.	5·08383	4·67374	91·933
12.	5·13372	4·71946	91·931
13.	5·16148	4·74190	91·929
14.	5·19919	4·77992	91·936
15.	5·37436	4·94088	91·934
		Average	91·933

Thus 100·000 parts of colourless argentic sulphate were found to yield 91·933 parts of argentic chloride, with a vanishingly small "probable error." If the weight of the darkened samples are used in the calculation the result becomes 91·934—a value which certainly represents the maximum. To have reduced the chief uncertainty to within such narrow limits was to have solved the problem as far as it need be solved at present. The interpretation of the result alone remains.

In comparing this result with that of Stas on argentic sulphate, it may be noted that Stas found in silver sulphate 69·203 per cent of silver. Because Richards and Wells found in argentic chloride $\frac{100·000}{132·867}$ 100 = 75·2632 per cent, it is clear that our results indicate 0·91933 × 75·2632 = 69·192 per cent of silver in silver sulphate, or 0·011 less than Stas's, one is forced to the conclusion that Stas's argentic sulphate was not completely reduced by hydrogen, and that his silver obtained in this way was no purer than the silver used in his other work. The only test of complete reduction used at the time was the solution of the residual metal in nitric acid; but this test could not reveal undecomposed sulphate and might not reveal traces of sulphide.

The Atomic Weight of Sulphur.

The interpretation of the new results is very similar to that already discussed in the paper on nitrogen and silver (CHEMICAL NEWS, xcvi., 180). In this case, as in that, there are two uncertain ratios; and one of these ratios, namely, that of silver to oxygen, occurs in each. In the present case, the other uncertain ratio is that of sulphur to oxygen, while in the former case the other uncertain ratio was that of nitrogen to oxygen.

In order to obtain a complete solution of the numerical relations in either of these cases, it is therefore obviously necessary to obtain another series of results, bringing in such a ratio as that of silver to sulphur, or oxygen to sulphur, or chlorine to oxygen. Such an additional ratio is not known at present with modern accuracy. Because of the fact that silver and oxygen are concerned in each of

the cases, a single new result, properly chosen, will solve both problems at once: but of course many new results with different compounds, confirming one another, are greatly to be desired. As has been said in the previous paper, some of these are already in the process of determination at Harvard College, and it is intended to pursue the matter further at the University of Berlin as well.

For the present it is necessary to state the interpretation of the results in a conditional manner, assuming various possible ratios between oxygen and silver, and stating the corresponding values for sulphur. In the future, when the assumed relationship is replaced by knowledge of the facts, intelligent choice can be made between the alternatives.

If oxygen is taken as 16·000, the following table gives the atomic weights of sulphur corresponding to the several atomic weights of silver.

Atomic Weight of Sulphur.

If Ag = 107·930 and Cl = 35·473, S = *32·113*
If Ag = 107·890 and Cl = 35·460, S = *32·078*
If Ag = 107 880 and Cl = 35·457, S = *32·069*

The lowest value in this case, as well as in the case of nitrogen, is the one supported by the recent work on the densities of gases.

In conclusion, it is a pleasure to acknowledge the generous assistance of the Carnegie Institution of Washington, without which the present work could not have been performed.

Summary.

The most important results of the research may be briefly summed up as follows:—

1. A method for the preparation of pure argentic sulphate was devised.

2. The specific gravity of argentic sulphate (previously fused) was found to be 5·45.

3. Indication was obtained that Stas was unable wholly to reduce silver sulphate in hydrogen.

4. Argentic sulphate was found to be occluded by silver chloride from solutions containing an excess of sulphuric acid.

5. It was proved that argentic sulphate can be completely converted into silver chloride by heating in a current of hydrochloric acid gas.

6. 100·000 parts of argentic sulphate were thus found to yield 91·933 parts of argentic chloride.

7. The atomic weight of sulphur as calculated from this ratio, if oxygen is taken as 16·000, with several assumed values for silver is—

Ag = 107·93	S = *32·113*
Ag = 107·89	S = *32·078*
Ag = 107·88	S = *32·069*

Attention is called also to the summaries of the three previous papers (Chemical News, vol. xcvi., pp. 148, 172, and 193).

Crystallised Iron Methylates.—K. A. Hofmann and Günther Bugge.—Methyl alcohol readily forms crystalline stable ferrites in the presence of acids, such as acetic or formic acid. Ethyl alcohol also possesses the same property to a less degree. Dimethoxyferric formate, $(CH_3O)_2FeO_2CH$, can be prepared by dissolving iron wire in strong formic acid and extracting the ferroformate obtained with methyl alcohol in an atmosphere of carbon dioxide. When the filtrate is exposed to the action of the air a yellow powder is precipitated. This powder consists of pointed double-refracting prisms of $(CH_3O)_2FeO_2CH$. Dimethoxyferric acetate, $(CH_3O)_2FeO_2C.CH_3$, is prepared similarly, using ferrous acetate instead of formate. When ethyl alcohol is used instead of methyl alcohol the solutions are, as before, readily oxidised in the air, but the products are very soluble. If the solutions are evaporated *in vacuo* a red powder remains behind, which contains only one ethoxy group, *i.e.*, the formula is $C_2H_5O.Fe(O_2C.CH_3)_2$.—*Berichte*, xl., No. 13.

USE OF FELSPATHIC ROCKS AS FERTILISERS.

By ALLERTON S. CUSHMAN,
Assistant Director, Office of Public Roads, and Collaborator, Bureau of Plant Industry.

(Continued from p. 207).

The Availability of Potash in Ground Rock.

The attention of the writer was first turned to the availability of potash in ground rock by a study of the decomposition which takes place when various rocks are used to form the surface of macadam roads. The binding power of rock dust depends upon the decomposition of the particles under the action of water and other substances. It has always been believed heretofore that only the potash that could be leached or dissolved out of a finely-ground material with water was available for plant growth. As a matter of fact, even the most finely-ground felspar which it is possible to obtain yields extremely minute quantities of potash to actual solution in water. Felspar which contained about 10 per cent of potash and was ground to a very fine powder yielded only 0·025 per cent to solution in water, and only 0·036 per cent to the action of a dilute acid. A large number of similar observations has led to the confident belief, almost universally held for many years, that although rocks which were disintegrated by natural processes served as the original source of potash, the action was so slow that it would be useless to grind rocks and attempt to use them as fertilisers. In the writer's investigations, however, evidence has been obtained which seems to show that decomposition of fine-ground felspar goes much farther than was indicated by the simple solution tests with water and dilute acids. By the use of laboratory methods it has been shown that almost complete decomposition can be made to take place in comparatively short periods of time under the action of water alone. In order to accomplish this result it has been necessary to use a method by which the potash is continually removed as fast as it is set free from its combinations in the rock. Now, as the roots of plants are continually performing this function, it is possible that in nature the decomposition of the felspathic particles in the soil must be continually going on as long as the product is being used, and slowing down to the stopping point when no removal is effected by plant growth. For further information on the scientific discussion of the decomposition of the felspars the original papers should be consulted (*Bull.* 92, Bureau of Chemistry, U.S. Dept. of Agriculture; *Cir.* 38 and *Bull.* 28, Office of Public Roads).

The fact, frequently cited and familiar to almost every person, that rocky hillsides with little or no soil can support growths of timber, would appear to demonstrate that rock potash is available. When it is remembered that wood ashes contain anywhere from 5 to 12 per cent of potash, it will be seen that a large tree represents, as it stands, a considerable quantity of this substance. However, trees take a long time to grow, and this present inquiry is mainly confined to availability in a single year from finely ground material.

In order to put the availability of the potash in very finely ground felspathic rocks to actual test the writer undertook some preliminary experiments in the greenhouse. Tobacco was selected for the experiments because, besides being extremely dependent upon an abundant potash supply, this plant is particularly well adapted to observation and control. Artificial soils were made up of clear, close-grained white sand and finely ground felspar, running about 8 per cent potash, such as is ordinarily prepared for use in the potteries, and which will pass through a standard sieve of about 200 meshes to the linear inch, having apertures approximately 0·0024 inch square. Tobacco seedlings were set out in this mixture and carefully fed from day to day with dilute solutions of ammonium nitrate and ammonium phosphate in order to supply the necessary amount of nitrogen and phosphoric acid. In addition to

* From *Bulletin* No. 104, U.S. Department of Agriculture, Bureau of Plant Industry.

this, a small amount of salts, containing lime, magnesia, and iron, was also added to the food solutions. Every care was taken, however, to see that no potash, except that which might be supplied by the felspar, obtained access to the plants.

For the sake of comparison, plants were also grown at the same time in a rich composted loam soil, which contained an abundance of all plant foods, including potash. Although the artificial sand-felspar soil was hard and apparently unsuited to the growth of plants, the tobacco nevertheless throve well in it, and showed at no time the slightest indication of potash starvation. When the experiments were finally abandoned, the tobacco plants growing in the sand felspar had attained a height of about 3 feet, and showed every indication of being as perfectly nourished as those growing in the rich soil.

In addition to the above experiments, seedlings were also set out in a poor, unfertilised soil, with and without the addition and admixture of a certain proportion of the ground felspar. Here also the availability of the felspar potash was clearly indicated.

These experiments, which were made in the summer of 1905, were not considered conclusive, but were sufficiently encouraging to justify further and more systematic investigation. Before proceeding it was of course necessary to look up the literature of the subject, in order to see to what extent ground felspar had been experimented with by other investigators. A Bulletin of the United States Department of Agriculture, which appeared a short time after the conclusion of the preliminary experiments described above, contains a partial reference list of previous publications along this line (*Bull.* 30, Bureau of Soils, U.S. Dept. Agriculture, p. 26).

On account of the great interest which has been aroused in this important subject and in order to present all the facts in the most accurate manner, the work of previous experimenters will be given in as much detail as space will permit. It is the intention to bring together all the information and evidence that the literature of the subject affords, whether it appears to be favourable to the use of ground felspar, or the reverse.

In 1849 Salm-Horstmar published in a German scientific journal (*Journ. Prakt. Chem.*, 1849, xlvi., 193) a method of preparing an artificial soil which, while being open, porous, and of a soft texture, should be absolutely free from all plant foods except those which were purposely added to it. The purest crystallised sugar was burned to a light form of charcoal and found to be absolutely free from any impurity capable of furnishing nourishment to plants. All sorts of different substances were then added to this material in other pots, and plants grown in them. In this way the experiments were kept under accurate observation and much information was obtained of the actual foods, and their forms, which are necessary to carry on the nourishment of plants. A short time after this investigation, in 1850, a chemist named Magnus repeated these experiments, and also made others (*Journ. Prakt. Chem.*, 1850, l., 65). In addition to the pots filled with sugar-charcoal, some of the pots were filled with coarsely pulverised felspar. It was found that the plants growing in the felspar made a good growth, even if no other food containing potash was added. The finer the felspar was ground the better was the development of the plants. Magnus summed up the results of his investigations as follows :—

1. In the absence of all mineral plant foods, barley attained a height of about 5 inches only before dying.
2. The addition of very small amounts of mineral plant foods enabled the plants to reach complete development.
3. If too much plant food was present, the plants were stunted or refused to grow at all.
4. In pure felspar barley made complete development and matured grain.
5. The development of growth varied with the coarseness or fineness of the felspar.

In 1861 Reichardt, a distinguished agricultural chemist, advanced the opinion that granite, porphyry, and other rocks rich in orthoclase felspar quickly give up their potash to plants when the particles are very fine ("Ackerbau Chemie," 1861).

About 1884 Hensel, a German writer and chemist, advocated the use of ground rock or so-called "stone meal," not only in order to supply the requisite potash, but also the phosphates and other mineral plant foods, such as lime, magnesia, iron, and manganese (A. J. Tafel, "Bread from Stones," 1894). This author published a philosophical work entitled "Das Leben," which treated in part of the use of rock fertilisers. Hensel thought that the use of excreta, offal, and other decaying and waste material as manure was harmful, if not to plants, at least to animals and men who subsisted upon them. Like many enthusiasts, Hensel appears to have been completely carried away by his ideas, which were not always justified by known facts. Hensel obtained, nevertheless, a considerable following and factories were established to prepare stone meal (Pomol, *Monatshefte*, No. 1, 1892; also *Wegweiser zur Gesundheit*, September 15, 1891). The subject evoked much discussion in Germany for many years. Whether rightly or wrongly, Hensel's ideas provoked the antagonism of nearly all the leading exponents of agricultural science in Germany. A great many experiments were undertaken, and in many cases the stone meal as prepared by the factories were shown to be very low in plant foods and nearly worthless as a fertiliser.

Among the prominent agricultural chemists who waged war on Hensel's stone meal were Wagner (*Zeit. Landw. Vereine Hessen*, 1894, lxiv., 14), Böttcher (*Centbl. Ag. Chem.*, 1895, xxiv., 363), Steglich (*Ibid.*, 1895, xxiv., 423), Hentschel (*Ibid.*, 1896, xxv., 136), Pfeiffer and Hansen (*Ibid.*, 1896, xxv., 802), and Morgen (*Ibid.*, 1898, xxvii., 743).

In some respects Hensel's arguments were not without weight, and he was keenly aware of the necessity for very fine grinding before the mineral constituents of rocks could be considered as practically available. The following quotation from a translation of Hensel's work stands for itself (A. J. Tafel, "Bread from Stones," 1894, p. 53).

"The practical point to settle is how far fertilising with stone meal pays, what yields it will afford; thus, whether it will be profitable for the farmer to use it. . . . It must here be premised that the fineness of the stamping or grinding and the most complete intermixture of the constituent parts are of the greatest importance for securing the greatest benefit of stone-meal fertilising. A manufactured article of this kind has recently been submitted to me which showed in a sieve of modern fineness three-fourths of the weight in coarse residuum. But as the solubility of the stone meal, and thus its efficiency, increases in proportion to its fineness, the greatest possible circumspection is required in grinding it. The finer the stone dust the more energetically can the dissolving moisture of the soil and the oxygen and nitrogen of the air act upon it. A grain of stone dust of moderate fineness may be reduced in a mortar of agate perhaps into twenty little particles, and then every little particle may be rendered accessible to the water and the air, and can, therefore, be used as plant food. Thence it follows that one single load of the very finest stone meal will do as much as twenty loads of a coarser product, so that by reducing to the finest dust, the cost for freight and carriage and the use of horse and cart would amount to only one-twentieth. Therefore we can afford to pay unhesitatingly a higher price for the finest stone meal that has been passed through a sieve than for an article that may be not so much a fine powder but rather a kind of coarse sand."

Inasmuch as this bulletin is interested mainly with the inquiry concerning the use of fine-ground felspar or felspathic rocks known to be rich in potash, no greater space need be given the German stone meal discussion.

(To be continued).

NOTICES OF BOOKS.

A History of Chemistry. By Dr. HUGO BAUER. Translated by R. V. STANFORD, B.Sc. (Lond.). London: Edward Arnold. 1907.

A SHORT history of chemistry containing in small compass, and at a moderate price, a complete account of the growth of the science from the earliest times to the present day will find a ready acceptance among those students who have not time for the study of the larger treatises on the subject, and Dr. Bauer's book will be found in many respects a useful addition to the chemists' library. It is well written, in simple and interesting language, and all the more important branches of the subject are at any rate touched upon. The chief defect is a want of balance with regard to the amount of space devoted to different periods and aspects of the science. Although the early years of its development are full of interest, the importance of the achievements of investigators before the time of Lavoisier would not, generally speaking, warrant the devotion of much space to their work and theories, when space is precious, while biographies of doubtful authenticity of early chemists, though they may add to the vividness of the narration, are not really worth the study of the young student. If the Periodic System cannot be accorded more than one page, twice this amount is too much to give to the biography of Paracelsus. Moreover, no accounts are given of the lives of many eminent modern workers, whose names are known all over the world, and, on the whole, too little attention is paid to the developments of recent years.

Précis d'Analyse Chimique Biologique Générale. ("Summary of General Biochemical Analysis"). By E. BARRAL. Paris: J. B. Baillière et Fils. 1908.

THIS work is a practical manual for physiologists, doctors, and chemists, describing methods of determining in the laboratory the substances contained in the organic tissues and liquids. Beginning with the albumenoids and going on to various nitrogenous derivatives, carbohydrates, fatty acids, &c., the general properties of each important substance, its characteristic reactions and methods of detection and determination are given. In every case the author has selected those methods which appear to him to combine simplicity with accuracy, and his experience of biochemical analysis enables him to give his readers a useful survey of the outlines of the subject upon which a detailed study of one or more of its branches could be based. Medical students in particular will find that the use of the book will enable them to economise in the time they give to the study of chemistry, because while they will avoid doing any general analysis which has no special bearing upon their medical work, nevertheless by the thorough investigation of animal products and tissues they will get an acquaintance with the manipulation and processes of analytical chemistry.

The Port of London and the Thames Barrage. By T. W. BARBER, M.Inst.C.E., and by C. J. DIBDIN, F.I.C., F.C.S., F.R.M.S., &c., E. T. HENNELL, M.Inst.C.E., CLAYTON BEADLE, F.R.Met.Socy., F.C.S., D. URQUHART. London: Swan Sonnenschein and Co., Ltd. 1907.

THIS book contains a series of expert studies and reports upon the conditions prevailing in the tidal river and estuary of the Thames. These studies include full accounts of the investigations of the engineer to the Thames Barrage Committee on the engineering aspects of the proposals which have been put forward with regard to the Port of London; moreover, papers on the infiltration from the Thames, the sanitary conditions of the river, &c., have been contributed by various experts, and the trade of the port is discussed. The writers establish clearly the practicability of the proposal of the construction of a barrage across the river in the neighbourhood of Gravesend, and although some of the economic aspects of the case for the present have had to be put on one side, the book at any rate provides opportunity for the public to acquire some knowledge of the probable effects of the proposed scheme.

CORRESPONDENCE.

THE FRUIT OF THE *CELESTRUS SCANDENS* AND *SOLANUM DULCARUM*.

To the Editor of the Chemical News.

SIR,—With reference to Messrs. Wells and Reeder's article on the above subject (CHEMICAL NEWS, vol. xcvi., p. 199), I think it is well to note that, in England, *Solanum dulcamara* is known as the "woody nightshade," and *Atropa belladonna* is the "deadly nightshade." There is no doubt Messrs. Wells and Reeder mean what we know as "woody nightshade," as they mention clusters of cherry-coloured berries.—I am, &c.,

ALBERT R. THORNWELL.

Highfield Road, Blackheath, Birmingham,
October 26, 1907.

To the Editor of the Chemical News.

SIR,—In Messrs. Wells and Reeder's article, *Solanum dulcamara*, whilst properly described in the text, is confounded with the "deadly nightshade." *Solanum dulcamara* is the woody or bitter nightshade, and is by no means so poisonous as the true deadly nightshade, whose berries are large, round, dark purple, and solitary, instead of "growing in clusters," "cherry-coloured," and "elliptical."—I am., &c.,

J. W. GATEHOUSE, F.I.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

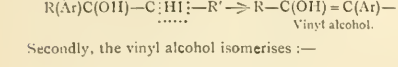
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 14, September 30, 1907.

This number contains no chemical matter.

No. 15, October 7, 1907.

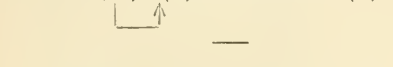
Migrations of Phenyl Group in Aromatic Iodohydrines by Elimination of Hydriodic Acid.—M. Tiffeneau.—The ethers of the aromatic iodohydrines (alkyliodohydrines, R(Ar)C(OAlk)—CHI—R') when treated with silver nitrate eliminate hydriodic acid and set free nitric acid, which hydrolyses the products of the transposition and converts them into aldehydes or ketones. Mercuric oxide, on the other hand, eliminates hydriodic acid, but leaves the medium neutral, and hence the products of the transposition are unaltered. Thus the author has proved that the transposition of these iodohydrines is effected in two stages. Firstly, the elimination of the

hydriodic acid causes the migration of the aromatic group, with the creation of a double bond:—



Vinyl alcohol.

Secondly, the vinyl alcohol isomerises:—



Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 13, 1907.

Cobaltic Dioximes.—L. Tschugaeff.—When dimethyl glyoxime acts on bromine pentammino bromide the reaction which occurs may be represented by the equation

$$[Co_5NH_3Br]Br_2 + 2DH_2 = [CoNH_3BrD_2H_2] + 2NH_4Br + 2NH_3.$$

The bromine compound formed is a typical non-electrolyte. On re-crystallisation from hot water containing some acetic acid it forms large reddish brown coloured glittering needles. Methyl ethyl glyoxime gives with xantho or isoxantho salts, $[Co_5NH_3NO_2]N_2$, a crystalline compound, $CoNH_3(NO_2)D_2H_2$, which also behaves like a typical non-electrolyte. From roseopentammino-iodide, $[Co_5NH_3H_2O]I_3$, an iodine compound of dimethyl glyoxime, $CoNH_3ID_2H_2$, has been prepared; it is not so stable as the corresponding chlorine and bromine compounds, but it is readily converted into the iodide of the diammino series, $[Co2NH_3D_2H_2]I$. The halogen compounds of the tetrammino series, $[Co_4NH_3Cl_2]Cl$ and $[Co_4NH_3Br_2]Br$, the praseo-salts; both react similarly with dimethyl glyoxime, but the isomeric croceo- and flavo-salts seem to behave differently. When a cobaltous salt reacts with dimethyl glyoxime in alcoholic solution in presence of pyridine an autoxidation process takes place, as represented by the equation—

$$2CoCl_2 + 4DH_2 + 4Py + O = 2[CoPyClD_2H_2] + 2PyHCl + H_2O.$$

This reaction also occurs in presence of *a*-picoline and other bases. In all the cases investigated brown or red-brown crystalline substances were obtained. They were usually hardly soluble in ordinary solvents (including water), and possess the properties of typical non-electrolytes.

Reductions with Amorphous Phosphorus.—Th. Weyl.—Under ordinary pressure phosphorus and hydrochloric acid have very little action on nitrobenzene at 100°, or even at 140°. In closed tubes, however, large quantities of bases are formed. These bases include aniline and also a good yield of solid *p*-chlor-aniline, rising to 75 per cent of the amount of nitrobenzene undergoing the reaction. Thus chlorine enters into the nucleus. To explain this striking reaction the author treated aniline with phosphorus and hydrochloric acid of specific gravity 1·19 first in open vessels at 100°, then in bombs at 140°, 170° and 190° to 220°, the action being allowed to last for ten hours; *p*-chlor-aniline was never obtained. Then the same experiments were performed with *p*-chlornitrobenzene, but again a negative result was obtained. However, *p*-chloraniline is formed by the action of hydrochloric acid on phenyl hydroxylamine and on nitrosobenzene. As both substances are very probably formed as intermediate products in the reaction between phosphorus, hydrochloric acid, and nitrobenzene, it is most likely that the formation of *p*-chlor-aniline is to be ascribed to these intermediate products.

Quantitative Expulsion of Phosphoric Acid from its Salts in a Current of Chlorine Saturated with Carbon Tetrachloride.—P. Jannasch and W. Jilke.—The apparatus for generating chlorine consists of a round flask of 2 to 3 litres capacity, a tubulated flask connected with it, and filled with caustic soda to absorb the chlorine when the experiment is finished, and a washing cylinder filled with concentrated sulphuric acid. The chlorine is made from 200 grms. of potassium permanganate and concentrated commercial hydrochloric acid, which is allowed to drop on the dry salt. With this quantity of permanganate a regular current of chlorine can be obtained for six hours. During the first three hours the reaction proceeds in the cold, and for the last part of the time the flask has to be heated. The chlorine is passed into an Erlenmeyer flask, which is warmed on a water-bath, and into which the carbon tetrachloride is allowed to drop slowly. The current of gases is then passed over the phosphate in a platinum boat heated in a combustion furnace, and the products received in water containing dilute nitric acid. After the combustion is over the liquid is collected in a porcelain dish, heated gently to drive off carbon tetrachloride, and then evaporated to a syrup. This is diluted and filtered, and the phosphoric acid present determined with molybdate.

Action of Sulphuric Acid on Phenol.—Jul. Obermiller.—Kekulé showed that when concentrated sulphuric acid acts upon phenol, phenol ortho-sulphonic acid is at first formed, and is rapidly converted into the *p*-acid on warming. These acids the author finds can easily be separated by converting them into mono-barium salts ($(SO_3H$-salts). On evaporating the aqueous solution of these salts and cooling the concentrated liquid, the salt of the ortho-acid crystallises out first, and from the mother-liquor the mono-magnesium salt of the para-acid crystallises when magnesium sulphate is added. The acids can also be separated by a method based upon the different solubilities of the mono-magnesium salts. If the raw mixture of sulpho-acids is first converted into mono-magnesium salt and evaporated at a low temperature most of the *p*-acid crystallises out. The mother-liquor then gives with magnesia an alkaline OH-magnesium salt of the ortho-acid. Similar OH-barium and aluminium salts can also be prepared. All three salts give a violet iron chloride reaction. The author has investigated the process of sulphonation in detail, and the most important result of his work is the proof that ortho-substitution is favoured by low temperatures and also by using as dilute acid as possible.

Compounds of Ethyl Carbylamine with Cobaltous Chloride, Ferrous Chloride, and Ferric Chloride.—K. A. Hofmann and Günther Bugge.—The authors' experiments show that cobalt and nickel, as well as platinum, in the form of chlorides are capable of yielding solid double cyanides. They have prepared the following compounds in the crystalline state:—(1) Cobaltous chloride-dis-ethylcarbylamine, $CoCl_2.2C_2H_5.NC$; (2) ferric chloride-dis-ethylcarbylamine, $FeCl_3.2C_2H_5.NC$; (3) ferric chloride-tris-phenylcarbylamine, $FeCl_3.3C_6H_5.NC$; (4) oxydiferric chloride-tetrakis-ethylcarbylamine, $OFe_2Cl_4.4C_2H_5.NC$; (5) oxydiferric chloride · pentakis · ethylcarbylamine, $OFe_2Cl_4.5C_2H_5.NC$.

Compounds of Salts of the Dichloro-chromium Base with Ammonium Salts.—R. F. Weinland and Theodor Schumann.—If ordinary green chromium chloride hydrate, $[CrCl_2(4H_2O)Cl.2H_2O$, is dissolved in a 35 per cent solution of ammonium sulphate, a green salt, $CrCl_3.2SO_4(NH_4)_2.6H_2O$, separates after a short time. In it one chlorine atom is dissociated in aqueous solution and precipitated by silver nitrate in nitric acid solution. The SO_4 is precipitated by barium chloride. This salt corresponds to Werner's double salt of chromium chloride and cæsium chloride, $CrCl_3.2CsCl.4H_2O$. According to Werner, the two molecules of cæsium chloride take the place of two molecules of water of the hydrate which have escaped *in vacuo* over sulphuric acid. The ammonium sulphate double salt contains two molecules of ammonium sulphate, and should thus contain only four molecules of water in addition, whereas six are present; this might be

due to the sulphuric acid, for sulphates contain more water than can be explained by Werner's hydrate theory. However, a sulphate, $[CrCl_2.4H_2O]\frac{SO_4}{2}.(SO_4)_2(NH_4)_3H$, has been obtained by adding sulphuric acid to the solution of ammonium sulphate and chromic chloride. Moreover, an ammonium chloride chromic chloride obtained by the authors also contains six molecules of water.

New Plant Alkaloids.—Amé Pictet and G. Court.—The authors have studied the alkaloids which can be isolated from the five plants tobacco, black pepper, cultivated carrot, parsley, and cocoa, and find the presence of more or less completely hydrated pyrrol nuclei in all the bases obtained. This analogy in chemical composition seems to point to a common origin of these bases, and shows that they are the decomposition products of one and the same mother substance in which the pyrrol nucleus is present. Emil Fischer, Küster, and Nencki have shown that this nucleus is present in the molecule of albumen and chlorophyll, and since in the latter it is probably condensed with a reduced aromatic ring, forming an iso-indol complex, and since it is hardly probable that it would be readily split off from such a complex, it must be concluded that the pyrrol bases in these plants are formed from vegetable albumen. Moreover, probably these simple bases must be regarded as the proto-alkaloids, from which, by various transformations (methylation, condensation, &c.), complicated alkaloids are formed. Since the plants examined were chosen at random and belonged to five different families, possibly the formation of these bases is due to a general biochemical process which occurs in all plants.

Chemistry of Hydrosulphites.—A. Binz and Th. Marx. — Benzoyl chloride gives with potassium oxalate, sodium nitrite, and soda, *i.e.*, with easily decomposed bases, benzoic acid anhydride, $2C_6H_5.COCl + Na_2CO_3 = 2NaCl + CO_2 + (C_6H_5.CO)_2O$. The same reaction occurs in presence of pyridine. Sodium hydrosulphite also gives benzoic acid anhydride, but, if no pyridine is present, in addition benzoyl disulphide is obtained. When pyridine is present, a red crystalline base of formula $C_{11}H_{10}N_2S$ is also formed, as well as a yellow compound which can readily be converted into the red base. Hydrosulphite behaves partly by sulphoxalate and partly like sulphite. When sodium sulphite reacts with benzoyl chloride, benzoyl disulphide is not formed. Thus this is a sulphoxylate reaction. As sulphur always separates, it is probable that it also plays some part in the reaction. Sulphur itself has no action on benzoyl chloride at 230°, but sodium sulphide might be formed from the hydrosulphite, and then give rise to the following reaction:— $2C_6H_5.COCl + Na_2S + S = 2NaCl + (C_6H_5.CO)_2S_2$. Benzoic acid anhydride, the red and the yellow substances, are formed both from hydrosulphite and from sulphite. The red substance is very easily combustible; analysis shows that in it two pyridine residues and a sulphur atom are connected with one another. The rôle of the benzoyl chloride in the reaction has not been explained. The yellow base has the formula $C_{23}H_{16}N_4S_4O_6$, but it cannot be re-crystallised; it is either not taken up by ordinary solvents or else it is converted into the red base.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Royal Institution, 5. General Monthly Meeting.
Society of Chemical Industry, 8. "Determination of Indigotin in Indigo-yielding Plants," by C. Bergtheil and R. V. Briggs. "Analysis of Indigo and of the Dried Leaves of *Indigofera Arrecta* and *Indigofera Sumatrana*," by R. Gaunt, F. Thomas, and W. P. Bloxam.

WEDNESDAY, 6th.—Society of Public Analysts, 8. Discussion on the Sealing of Samples. Members and their friends will meet to dine at the Comedy Restaurant, Pantoo Street, Haymarket, at 6.15.

THURSDAY, 7th.—Chemical, 8.30. "Gaseous Nitrogen Trioxide," by H. B. and Miss M. Baker. "Atomic Weight of Tellurium," by H. B. Baker and A. H. Bennett. "Isomerism of the Double Sulphites of Sodium and Potassium," by M. H. Godby. "Studies in the Camphane Series—Part XXIV., Camphoryldithiocarbamic Acid and Camphorylthiocarbimide," by M. O. Forster and T. Jackson. "The Vapour pressures of Triethylamine, of *sym*-Trimethylpyridine, and their Mixtures with Water" and "Liquid Triethylamine," by R. T. Lattey. "Action of Sulphuretted Hydrogen on Solutions of Sodium Hydrosulphite," by F. S. Sinnatt. "Alkyl Compounds of Gold—Diethylauric Bromide," by W. J. Pope and C. S. Gibson. "Constitution of Homoeriodictyol," by F. B. Power and F. Tutin. "Interaction of Methylene Chloride and the Sodium Derivative of Ethyl Malonate," by F. Tutin. "Preparation of Aliphatic Nitro-compounds by the Interaction of the Alkyl Iodides and Mercurous Nitrite," by P. C. Ray and P. Neogi. "Some Mercury Derivatives of Camphor," by J. E. Marsh and R. de J. F. Struthers. "Chemistry of the Terpenes—II., The Oxidation of Limonene with Chromyl Chloride," by G. G. Henderson. "Synthesis of Acridines and Phenonaphthacridines—Tetra- and Hexa-methylacridines, Dimethylphenonaphthacridines, Dixylylmethylenediamines," by A. Senier and A. Compton.

FRIDAY, 8th.—Physical, 8. Discussion on Mr. Campbell's paper on the "Use of Variable Mutual Inductances." "A Graphic Method for Stream-lines and Equipotential Surfaces," by L. F. Richardson. "Lateral Vibrations of Bars supported at Two Points with one End Overhanging," by J. Morrow.

ERRATUM.—P. 188, col. 1, line 34, *for* "$6L_3$" *read* "bL_3."

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2502.

A NEW METHOD SUGGESTED FOR DETERMINING VAPOUR-DENSITIES.

By PHILIP BLACKMAN

The apparatus consists of a vessel having a tight-fitting stopper at one end and at the opposite end a long capillary tube with a tap at its end. (The tap is such that when turned off its "blade" is in line with the capillary). By means of a split cork it can be inserted in a flask fitted with a condenser (Fig. 1). The volume of the vessel is

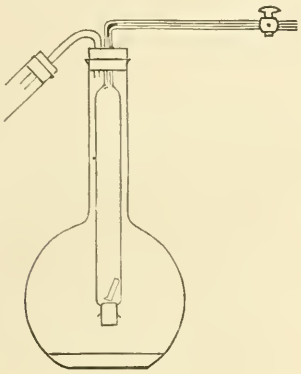


Fig. 1.

determined once for always, and also that of the capillary, the latter being graduated. A short thread of mercury is introduced to close the tap, and another near the body of the vessel; the air space between the two threads will serve as a pressure gauge. A weighed quantity of the substance to be experimented on is introduced in a small tube, the stopper fixed and tied firmly to the neck with wire, the whole fixed in the flask, and finally heated in the vapour of some liquid boiling at a temperature above the boiling-point of the substance (if water be employed as the heating liquid, the use of a condenser may be dispensed with). It will be observed that solid substances which can be vaporised can be dealt with by this method. The final readings are taken when the volume of the air in the gauge remains constant.

Let ρ = atmospheric pressure;
t_1 = initial temperature;
t_2 = temperature of vapour;
t_3 = mean temperature of the gauge;
t_4 = mean temperature of the space between the vessel and the first mercury thread;
L = initial volume of the air gauge;
l = final volume of the gauge;
H, h = respectively the initial and final volumes of the space between the vessel and the first mercury thread;
V = volume of the vessel;
w = weight of substance.

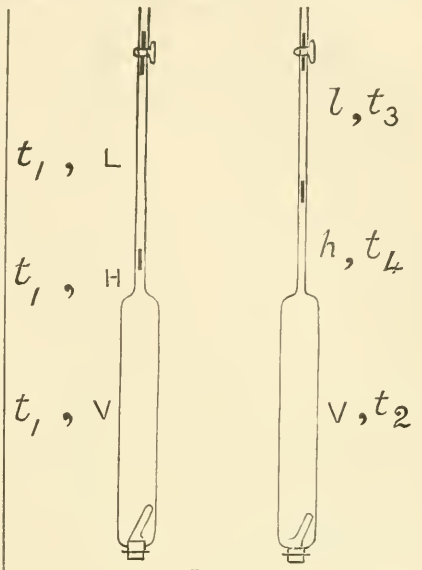


Fig. 2.

Pressure of air in gauge $= \rho L(273+t_3)/l(273+t_1)$; pressure of air in space $V = \rho(273+t_2)/(273+t_1)$; pressure of air in space $h = \rho H(273+t_4)/h(273+t_1)$; hence the pressure due to the vapour

$$= \frac{\rho}{273+t_1}\left[\frac{L}{l}(273+t_3) - (273+t_2) - \frac{H}{h}(273+t_4)\right] = \pi.$$

The volume of the vapour at 0° and 760 mm.

$$= \frac{\pi V\, 273}{760\,(273+t_2)} + \frac{\pi h\, 273}{760\,(273+t_4)} = v.$$

Therefore the density of the vapour at 0° and 760 mm.—

$$= \frac{w}{v}$$

$$= \frac{760\, w\,(273+t_1)}{273\rho\left(\frac{V}{273+t_2} + \frac{h}{273+t_4}\right)\left(\frac{L}{l}(273+t_3) - (273+t_2) - \frac{H}{h}(273+t_4)\right)}$$

From this a comparison with the vapour-density of hydrogen at 0° and 760 mm. may be made.

The calculation and manipulation will be much simplified if the apparatus be of the form shown in Fig. 3. (The apparatus shown in Fig. 4 has the advantages of greater sensitiveness of the air gauge due to its greater length and increased capacity of the volume V). The whole apparatus can thus be introduced into the vapour of the boiling liquid by suspending it with wire from the cork.

In this formula we have $t_2 = t_3 = t_4$, and the formula for the vapour density thus becomes—

$$\frac{760\, w\, l\,(273+t_1)}{273\,\rho\,(V+h)\left(L - l - \frac{H\,l}{h}\right)}.$$

In practice it should be found easy to so manipulate the

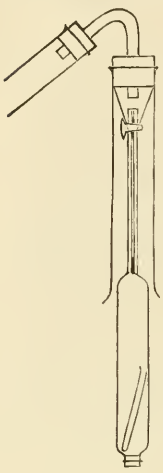


FIG. 3.

FIG. 4.

threads of mercury as to make H = o, and thus the formula last given becomes—

$$\frac{760\, w\, l\, (273 + t_1)}{273\, \rho\, (V + h)(L - l)},$$

or (as h is generally very small compared with V, and may thus be neglected for ordinary purposes)—

$$\frac{760\, w\, l\, (273 + t_1)}{273\, \rho\, V\, (L - l)}.$$

ON THE ELECTROLYSIS OF SALT SOLUTIONS IN LIQUEFIED SULPHUR DIOXIDE AT LOW TEMPERATURES.*

By BERTRAM D. STEELE, D.Sc.

THE investigation of which this is a preliminary notice is a natural continuation of the research started by Dr. M'Intosh and myself in 1903. The investigation has for its object the study of the electrolysis of salts dissolved in certain liquefied gases, and of the products formed during electrolysis. The first system that has been investigated is that of a solution of potassium iodide dissolved in sulphur dioxide, and a large number of experiments extending over several months have been carried out.

My attention having been called to a proposed investigation along similar lines by Giuseppe Magri, of which an abstract appears in the *Journal of the Chemical Society* (xcii., p. 237, April, 1907), I thought it best to publish the following brief summary of the conclusions that have been so far arrived at :—

1. When a nearly saturated solution of potassium iodide in sulphur dioxide is electrolysed between electrodes consisting of thin platinum wires, and with a potential difference of between 10 and 20 volts, a current of about 80 to 100 milliampères is obtained during the first instant. The current immediately begins to fall rapidly to a value considerably less than 1 milliampère. With a potential difference of about 40 volts apparent gas evolution occurs (possibly ebullition of sulphur dioxide), and on breaking the circuit a polarisation E.M.F. of over 1 volt is obtained.

2. With larger platinum electrodes the fall in current is much slower, but after several hours falls to a similar extremely low value. In this case a scarcely detectable polarisation voltage can be observed.

3. Similar results are obtained when mercury electrodes are used, but the fall in current is not so marked.

4. With platinum and mercury electrodes the current, which is extremely variable and inconstant, appears to depend on the previous history of the electrodes.

5. It has been found that a constant and consistent current can be obtained by using a silver, copper, or iron cathode of large area.

6. The following changes occur at the anode :—
   When a platinum anode is used iodine is liberated and dissolved in the surrounding solution.
   When a zinc anode is used no iodine is liberated, and the solution remains yellow in colour. It is probable that zinc iodide is formed and dissolved in the solution.
   When an iron anode is used no iodine is liberated, but the solution surrounding the anode becomes blackish green in colour.
   When a mercury anode is used mercurous iodide is formed and precipitated, forming a layer on the electrode which appears to cut off the current.

7. The following changes occur at the cathode :—
   When currents of 20 milliampères and over are used with a platinum cathode there is formed a dark coloured crystalline deposit, which on drying in an atmosphere of dry sulphur dioxide becomes white. Small quantities of sulphur are always found mixed with this deposit.
   The deposit on analysis was found to have a composition very closely corresponding with that required for potassium sulphite, in some cases being, however, much richer in sulphur dioxide.
   The platinum cathode, if very small currents are used, is still coated with the potassium sulphite compound, but contains little, if any, admixed sulphur, which is, however, in all cases found dissolved in the solution surrounding the cathode.
   The extraordinary manner in which the current falls after the first few moments is thus accounted for by the deposition of a thin film of insulating sulphur on the surface of the cathode.
   The deposition of sulphur is prevented by using either a silver or a copper cathode. Under these circumstances a black deposit is formed on the cathode. This deposit is probably silver sulphide or copper sulphide, as the case may be, and as both of these are conducting substances the current is not seriously diminished.
   No evidence has yet been obtained of the deposition of potassium as metal on the cathode.

8. By means of a specially constructed piece of apparatus the conductivity of the solution in the neighbourhood of the cathode was determined during the progress of the experiment, and in all cases an increase of resistance was observed.

In the same way as the liberation of hydrogen at the cathode during the electrolysis of a solution of potassium iodide in water is regarded as evidence of the occurrence of hydrogen cations in the aqueous solution, so the liberation of sulphur at the cathode in the foregoing experiments indicates the occurrence of sulphur cations in a solution of potassium iodide in sulphur dioxide, and similarly the formation of what is probably potassium sulphite in the latter system is analogous to the formation of potassium hydroxide in the former.

* A Paper read before the Faraday Society, October 29th, 1907.

The following is a possible representation of the changes which take place :—

$$S:: + 4\Theta = S$$
$$4K^{\cdot} + 2O'' + SO_2 = 2K_2SO_3.$$

the sulphur and the potassium sulphite being deposited together at the cathode.

This would explain not only the formation of these two substances but also the observed diminution in conductivity of the solution immediately surrounding the cathode.

9. After the necessary conditions for obtaining a steady current had been worked out, a special apparatus was designed and constructed for the measurement of ionic velocities of the ions in sulphur dioxide solution, and a few preliminary measurements have been made with this apparatus.

It is intended to extend these measurements and to thoroughly investigate this and other similar systems.

NOTE ON THE

SOLUBILITY OF BISULPHITE COMPOUNDS OF ALDEHYDES AND KETONES.

By JOHN B. COPPOCK, B.Sc. (Lond.), F.I.C., F.C.S.

It has been noticed that students working the bisulphite reactions for the lower aldehydes and ketones fail to get the usual precipitates, consisting of the bisulphite and the aldehyde, or ketone, if a solution of the bisulphite be made by saturating a sodium carbonate solution with sulphur dioxide gas. The solution used has been a saturated one of the bisulphite, made as above, and having a deep yellow, much like potassium chromate solution.

If, on the other hand, a saturated solution of the bisulphite, made by dissolving this salt in hot water and then cooling, be added to the compounds under consideration the usual precipitate is obtained.

This difference suggested the probability of the compounds being soluble in sulphur dioxide ; to see if this is the explanation the following experiments were made :—

Acetaldehyde.—Saturated solution of bisulphite added, and precipitate obtained. The precipitate, with the solution, was subjected to a stream of sulphur dioxide gas, when it finally dissolved.

Acetone.—This was treated precisely as above, and sulphur dioxide on being passed again dissolved the precipitate.

The precipitates were also subjected to a golden yellow solution made as described in the first paragraph ; this in each case dissolved the precipitate.

Very plainly it seems that in making a saturated solution of a bisulphite from washing soda the sulphur dioxide gas should not be passed until the liquid is strongly smelling of it. A very pale green tint seems to be the point where the sulphur dioxide should be cut off.

Chemical Laboratory, Kendal.

FURTHER ANALYSES OF CONDENSED MILK.

Report by F. J. LLOYD, F.C.S., Consulting Chemist to the British Dairy Farmers' Association.

When I received instructions to make analyses of another five samples of condensed milk, and this time not to confine myself to machine-skimmed milk, I endeavoured to obtain samples of full-cream milk from the same sources as I had obtained the machine-skimmed. It must be clearly remembered that I had not bought these former samples as or knowing them to be machine-skimmed, but had simply asked for the brands of which they sold the greatest amount, and it was only after purchasing the samples that I found in all cases they were machine-skimmed. Now upon attempting to obtain samples of full-cream milk I was met with two difficulties : First, that in many of these places nothing whatever was kept but condensed machine-skimmed milk ; and, secondly, that after numerous efforts in various places I could only find three full-cream condensed milks on the market. Subsequently I obtained Sample A 89 (unsweetened), and also Sample A 88, which I had not previously examined, and which appears to be the cheapest machine-skimmed milk on the market. It is only fair to state that the makers of this brand print on the label surrounding the tin—"Unsuitable for the use of infants and invalids."

As regards the composition of the samples themselves, nothing need be said ; they all represent milk reduced to about one-third its volume, so that to bring it back to the richness of ordinary milk as regards fat and other solids, one part of these milks could be mixed with only two parts of water. It will be seen that, even taking the first two samples, 45 ozs. of milk would cost 5½d., *i.e.*, for a little over a quart of milk, which is a much higher price than the same quantity of milk can be bought for in a fresh condition. There can, I think, be no doubt whatever that the people who use condensed milk dilute it to such an extent that it becomes practically a mixture of equal parts of milk and water. Indeed, on one of the tins the directions state that for puddings, coffee, tea, &c., the milk may be diluted with four or five times its volume of water.

	A 85.	A 86.	A 87.	A 88.	A 89.
Nature	Full cream	Unskimmed Swiss	Full cream	Machine skimmed	Full cream, unsweetened
Prepared in	England	Switzerland	Switzerland	Holland	Norway
Contents of tin	15 ozs.	15 ozs.	14½ ozs.	13 ozs.	12 ozs.
Price of tin	5½d.	5½d.	5½d.	2d.	4½d.
Analysis—Water.. ..	18·70	13·04	16·52	26·14	67·72
Fat	9·94	11·13	8·20	1·02	10·13
Casein . ..	10·95	8·37	9·90	8·43	10·86
Sugar, &c...	58·21	65·46	62·54	62·41	9·55
Ash	2·20	2·00	2·84	2·00	1·74
	100·00	100·00	100·00	100·00	100·00
Containing boric acid..	0·17	0·10	None	None	None

The Society might endeavour to discover how far the condensed milk used in or imported into England consists of full-cream or machine-skimmed milk. I think also that some steps should be taken to draw the attention of the medical profession to the composition of condensed milk, and to the danger which must arise from infants being fed upon it. Probably much of the ill-health among children, frequently attributed to the consumption of impure fresh milk, if investigated, would be found to be due to the use of condensed machine-skimmed milk. It is very doubtful whether the vast majority of the poor people who buy and use this condensed machine-skimmed milk have any knowledge of what they are using. They simply buy what is cheapest, and make it go as far as they possibly can, without any regard to the health of their infants.

Laboratory.
Muscovy House, Trinity Square, London, E.C.,
September, 1907.

THE

USE OF FELSPATHIC ROCKS AS FERTILISERS.*

By ALLERTON S. CUSHMAN,
Assistant Director, Office of Public Roads, and Collaborator, Bureau of Plant Industry.

(Continued from p. 219).

The Availability of Potash in Ground Rock (continued).

Some experiments were carried out in 1887 on the use of ground felspar as a fertiliser by Aitken, a Scotch agriculturist, and chemist to the Highland and Agricultural Society of Scotland. Aitken does not say that he was aware of the work of Magnus or the deductions of Hensel. The record of these experiments is given in the author's own words (*Trans. Highland and Ag. Soc. Scotland*, 1887, Series 4, xix., 253) :—

"We are familiar with the fact that felspar, under the slow but constant action of those forces included under the name of weathering, becomes disintegrated and decomposed, and that the potash it contains is dissolved away from it by rain, so that streams emanating from districts where felspathic rocks abound are found to contain potash salts, and the level straths laid down by the prolonged action of these streams yield fertile soils that are rich in potash. These soils are the product of natural agencies that have been going on for centuries, and the store of soluble potash salts they contain has been increased to an untold extent by the slow solvent action of the roots of plants that have grown on them, so that the conversion of felspathic rock into soil so rich in potash as to afford an abundant supply of that constituent for the raising of agricultural crops is the product of the work of centuries. At first sight, it might seem a foolish thing to expect that by merely grinding felspathic rock, and strewing the powder upon soils deficient in potash, the long natural process referred to should be so accelerated as to cause the felspar to act as a source of potash for the immediate use of the growing of crops whose vigorous growth demands a relatively large amount of that substance. Nevertheless, the striking results of an experiment made at the Society's experiment station at Pumpherston showed that such an expectation was not altogether unreasonable. Ground phosphates had been used as a phosphatic manure with varying success for some years, and as it seemed that the varying nature of the results obtained might be due to the varying degrees of fineness to which phosphates were ground, I made a small preliminary experiment, in which the same phosphate was applied in different degrees of fineness, and I found that the more finely ground the phosphate the more effective was it as a manure. A similar experiment on a larger scale is described in the *Transactions*, p. 245, where it is seen that the efficiency of ground phosphates is in direct proportion to their fineness. It therefore seemed reasonable to suppose that felspar, although it is a very insoluble substance, might, if it were ground to an exceedingly fine powder in certain circumstances, be found to yield to the action of the solvents in the soil and in the roots of plants so rapidly as to be available as a source of potash to some crops, even during the short period of a single season.

"Accordingly I obtained, through Mr. Bödker, the Swedish and Norwegian consul here, at whose instigation the experiment was undertaken, a supply of very pure felspathic rock, rich in potash, of which enormous quantities are to be had in Norway. It was ground as finely as possible by Messrs. J. & J. Cunningham, of Leith, and thereafter sifted through a sieve of 120 wires to the linear inch and was found to contain about 12 per cent of potash. The whole quantity of sifted felspar was very small, less than a half hundredweight, and as it was received late in the season, the experiment was made simply to afford information which might indicate whether it was desirable to try the experiment on a larger scale the following season. There were two small experiments made—one by Mr. R. Shirra Gibb, at Boon, on a crop of peas, and one at Pumpherston on turnips. The experiments were on plots of one-fortieth acre, and the following were the manures employed and the results obtained :—

	Kind and quantity of fertilisers.	Peas. Dried in bulk. Lbs.	Peas. Grain. Lbs.	Turnips. Bulbs. Lbs.
1	Sulphate of potash, 3 lbs. Sulphate of lime, 3 lbs. .. Superphosphate, 6 lbs. ..	114	3·8	482
2	Ground felspar, 12 lbs. .. Sulphate of lime, 3 lbs. .. Superphosphate, 6 lbs. ..	102	3·5	496
3	Sulphate of lime, 3 lbs. .. Superphosphate, 6 lbs. ..	96	—	476

"Although the whole experiment is on a small scale, and the crops are below the average, there is nevertheless a clear indication that the felspar has acted as a potash manure. In both cases where no potash was applied the crop is the smallest. At Boon the plot with no potash was unable to mature its seed, so that it could not be thrashed, while on the other two plots the amount of seed was not very different, and quite in proportion to the total crop, viz., about one-fortieth. The smallness of the crop does not detract from the value of the experiment as a means of indicating whether or not felspar acts as a potash manure. Had the crop been sown at the proper time it would have been much larger. In the case of the turnip crop the ground felspar has done better than the sulphate of potash. That may be accidental, but it may be that the insoluble form in which potash is contained in felspar is more favourable for turnip growing than the soluble sulphate. Soluble potash manures, when applied to the turnip crop, sometimes diminish rather than increase the crop, and this is especially the case where the crop is dunged in the drills; but no dung has been put on the Pumpherston station these twelve years, and the results obtained all over the field show that potash is now required for turnip growing on that land.

"Upon the whole, the result of this experiment may be taken as showing that potash felspar when ground to an exceedingly fine powder is capable of acting as a potash manure even in a single season."

In 1889 the Maine State experiment station, under Balentine, independently of any previous experimenters, investigated the use of ground felspar as a source of potash on oats ("Annual Report Maine State Col. Exp. Station," 1889, p. 143). The results are given verbatim from the records of the station :—

"In connection with the experiments with finely ground phosphatic rock as a source of phosphoric acid for plants, pot experiments have been undertaken to determine to what extent plants can avail themselves of the potash of potash felspars. The pots used for the experiments were like those used in the phosphate experiments. They were also filled in the same manner, having first a layer of gravel at the bottom and above this 65 pounds of quartz sand, with the last 35 pounds of which were mixed the experimental fertilisers.

"Three pots, 1, 5, and 9, were supplied each with 10 grms. of felspar carrying 11·61 per cent of potash, 10 grms. of nitrate of soda, and 10 grms. of acid South Carolina rock. Three other pots, 13, 17, and 20, were fertilised with 20 grms. of felspar and the same amount of nitrate of soda and acid phosphate as was supplied to 1, 5, and 9. In these pots were planted oats. When the oats were 2 or 3 inches high they were thinned out to 18 plants per pot. The pots were watered in the same manner as were those in which the experiment with phosphates was conducted.

* From *Bulletin* No. 104, U.S. Department of Agriculture, Bureau of Plant Industry.

TABLE A.—*Weight of Crop of Oats from Seven Plats of 100 Plants each, Grown with various Fertilisers.*

No.	Kind of Fertiliser	Grain. Grms.	Straw. Grms.	Chaff. Grms.	Total. Grms.	Equivalent yield of grain per hectare. Kilogrms.
1.	Unfertilised	5·3	11·0	1·0	17·3	216
2.	Phosphate and potassium sulphate	157·3	220·5	16·3	394·1	6400
3.	Phosphate and 300 felspar potash	133·8	178·7	15·5	328·0	5450
4.	Phosphate and Chili saltpetre	175·5	242·8	21·2	439·5	7150
5.	Phosphate, Chili saltpetre, and potassium sulphate	232·5	346·2	24·8	603·5	9470
6.	Phosphate, Chili saltpetre, and 200 felspar potash	171·5	245·2	21·3	438·0	7000
7.	Phosphate, Chili saltpetre, and 300 felspar potash	177·7	262·5	23·5	463·7	7240

"In the table below are shown the results of substituting muriate of potash for felspar as a source of potash :—

Kind and quantity of fertilisers.	No. of pot.	Yield of grain. Grms.	Yield of straw. Grms.
10 grms. felspar	1	18·37	47
10 grms. nitrate of soda	5	14·37	43
10 grms. acid South Carolina rock	9	19·43	47
20 grms. felspar	13	17·28	47
10 grms. nitrate of soda	17	16·78	47
10 grms. acid South Carolina rock	21	16·83	52
3 grms. muriate of potash	16	22·88	67
10 grms. nitrate of soda	20	18·85	72
10 grms. acid South Carolina rock	24	24·37	65

"The pots receiving 10 grms. of felspar produced, on the average, about 79 per cent of the average of the grain produced by those pots receiving 3 grms. of muriate of potash having 50 per cent of actual potash. The amount of grain was not increased by increasing the felspar to 20 grms., though there was a slight gain in straw.

"The conclusion to be drawn from the expetiment is that the oats were able to draw from the felspar potash enough for a large crop of grain. If this conclusion is verified by future work, some of our felspars may prove a cheap source of potash to the farmers of the State."

Examination of the figures given in the above table shows that the potash from the felspar undoubtedly became available, but was not as efficient as that from the more soluble muriate.

In 1889, the same year that the results of these experiments were made public, Nilson in Sweden published an investigation in which fine-ground felspar prepared for the potteries was tested in comparison with potassium sulphate ("Landtbr. Akad. Handlingar och Tidskr.," 1889; see also *Centbl. Ag. Chem.*, 1889, xviii., 608). Oats were used, and the experiments were carried out on the Swedish moor soils, which, in a dry condition, already contained 0·5 per cent of potash, although only 0·03 per cent of this was soluble in dilute acid. There were 300 kilogrms. (660 pounds) of slag phosphate, 50 kilogrms. (110 pounds) of nitrogen in the form of Chili saltpetre, and 80 kilogrms. (176 pounds) of potash as sulphate or 200 to 300 kilogrms. 440 to 660 pounds) as ground felspar added to the hectare (2·47 acres). The results of weighings of crop yield, made on the basis of 100 plants from each trial, are given in Table A.

Nilson's results are most unfavourable to ground felspar, as an inspection of the figures shows, but as a very good yield was obtained by the use of Chili saltpetre and phosphate without any additional potash, the experiments are not very conclusive. Chili saltpetre is a crude nitrate of soda which sometimes contains potash salts. It is possible that in all these experiments there was a tendency to overfeeding rather than to underfeeding.

In 1890 Sestini published the results of a very interesting investigation of the decomposing action of plant roots on felspar (*Landw. Vers. Stat.*, 1900, liv., 147). A coarse felspathic granite sand from the island of Elba was first carefully washed to remove all adherent earth or plant food, and then mixed with certain amounts of carbonate, phosphate, and sulphate of lime. The nitrogen was supplied in the form of ammonium nitrate. Various plants and grasses were grown in this mixture under very careful test conditions. The crops matured well, and at the end of about a year it was shown that a very considerable decomposition of the felspar had taken place. Sestini concluded that the decomposition of the felspar went on much more rapidly under the influence of plant growth than had previously been supposed.

In 1901 Headden, working at the Colorado Experiment Station, also independently, carried on some interesting experiments on the availability of potash contained in ground felspar (Colorado Experiment Station, *Bull.* 65, p. 30). To quote this author's own words :—

"We endeavoured to determine whether the felspar could furnish potash to plants. For this purpose fresh mineral was used, pulverised as already described in imitation of the soil, *i.e.*, the particles varied from 1 mm. in diameter to an impalpable powder. This was mixed with pure quartz sand. Bone-ash was used to supply lime and phosphoric acid. The sample used contained no potash. Nitrate of lime furnished the nitrogen. Chlorine was furnished by a minute quantity of calcic chloride. Distilled water was used throughout the experiment.

"The plants grew healthily in this mixture until the floors of the building were oiled, and the room in which the plants were growing was shut up and became too warm; these two things together gave them a decided setback, and later a thrips, *Thrips striata* according to Prof. Gillette, attacked the plants, and did them much damage. Some of the plants, however, seeded. They were harvested, though in bad condition, and very uneven in the degree of their development. The root system was well developed, the sand being filled with the roots. The weight of the tops as harvested was 198·5 grms.; that of the roots as washed out was 40 grms. The tops and roots were incinerated together, and yielded 5·795 per cent of soluble and 9·803 per cent of insoluble ash, a total of 15·598 per cent.

"Examination of the felspars used showed the presence of 11·993 per cent of potash and 2·988 per cent of soda. Phosphoric and sulphuric acids were present in very small quantities; the former equalled 0·041 per cent and the latter 0·003 per cent of the felspar.

"The nitrogen in the oat hay, roots included, was 3·2543 per cent.

"The ash gave the following analysis :—

Carbon	0·17 per cent
Sand	8·13
Silicic acid	15·73
Sulphuric acid	4·41
Phosphoric acid	3·98
Carbonic acid	15·35
Chlorine	2·73
Potassic oxide	15·95
Sodic oxide	4·62
Calcic oxide	21·70
Magnesic oxide	3·90
Ferric oxide	0·96
Aluminic oxide	0·31
Manganic oxide	0·16
Ignition	2·61
	100·71

"This ash is very anomalous in its composition as well as in the quantity present in the plants. The plants were not evenly matured at the time of gathering, and were in bad condition. The question we endeavoured to investigate, however, is perfectly answered by the results, *i.e.*, the oat plant can use the finely-divided felspar as a source from which to obtain potash, for in this experiment, made under very adverse conditions, we found that the oat plants took from the felspar 1·4417 grms. of potash. The potash added in the seed has been deducted. The silicic acid appropriated by the plant indicates the decomposition of the silicate."

In 1905 Prianischnikow, a Russian investigator, published the results of a series of pot tests using felspar and mica as sources of potash (*Landw. Vers. Stat.*, 1905, lxiii., 151). The felspar used was ground so that it was less than 0·25 mm. in diameter, corresponding to an 80-mesh sieve. The material was mixed with sand, and the other foods added in the form of phosphates and nitrates of lime and soda. The cultures used were tobacco, buckwheat, flax, peas, sunflowers, and barley. The tabulated results are too voluminous for insertion here, but they appear to show that the felspar, even in large amounts, had little or no effect on the growth of the plants. The investigator concluded that mica is, if anything, a better source of potash than felspar, but that neither of these minerals supplies a sufficient quantity to make them worth the slighest consideration so far as plant growth is concerned. The only criticism of these experiments that might be offered is that 80-mesh felspar powder is far too coarse to be used in pot experiments. This point will be taken up more fully later on.

The most important researches which have ever been published tending to show that under certain conditions finely-ground felspar is worthless as a fertiliser are those of von Feilitzen (U.S. Dept. Agriculture, *Ex. Sta. Record*, 1904, xvi., 30). This experimenter, like Nilson, worked on Swedish moor soils. He concluded that ground felspar is almost worthless as a fertiliser. The results and conclusions are best shown by abstracting from a translation from von Feilitzen's publications ("How Deficiency in Potash Affects Clover and Timothy"):—

"Potash, as is well known, is one of the necessary constituents of plant food; consequently, if it is absent in the soil or only there in insufficient quantities, a normal development of the higher orders of plants is not possible. According to the researches of plant physiologists, it is particularly instrumental in the formation and transport of the carbohydrates (sugar, starch, &c.), for which reason potash plays such a prominent part in the manuring of potatoes, turnips, and other root crops, but it is also required for cereals and all the other cultivated plants. Of late, comprehensive experiments have been carried out by Prof. Dr. H. Wilfarth at the experimental station at Bernburg, with the view to ascertain in what way the want of one or several of the necessary constituents of plant food influenced the development and appearance of plants. On this occasion he found that the want of potash caused a defective growth of some of the vegetative parts, the leaves of potatoes, tobacco, buckwheat, and beetroots assuming a speckled appearance (*Journ. für Landw.*, 1903, No. 11). Certain clearly defined portions, especially at the borders of the leaves, grew yellowish white and decayed, while the other parts retained their original appearance. These marks are often very much like those caused by fungi and insects, but if examined more closely it becomes evident that they cannot be due to such causes.

"In 1903 we made quite similar observations, when experimenting with clover and timothy grass, and, as it should be of interest, I shall describe in short the observations made by us. In 1902 a series of experiments were prepared in plots of soil of 1 square metre each (about 1 yard square), charged with rather well-decayed reed grass turf, poor in potash, in order to investigate whether the potash in a mineral fertiliser, prepared in Sweden, was of any manurial value. As, by analysis, this fertiliser turned out to be finely-ground felspar, we were prepared for an unfavourable result at the very outset."

The fineness of the ground felspar is not given, but an analysis showed that it contained 8·15 per cent of potash. The experimental series was made up of two plats, each fertilised as shown in the following table, and in May, 1902, they were sown with a clover-grass mixture containing red clover, bastard clover (alsike), white clover, and timothy grass. Even in the first year the grass developed vigorously, and produced vegetable matter, as shown in the table. An average of 1 square metre of each of the two parallel plats was taken. Fifty-four pounds of phosphoric acid were used on each plat.

Plat No.	Kind and quantity of fertiliser per acre.	Green vegetable matter produced (average of 2 plats).	Increase due to potash (average of 2 plats).
		Pounds.	Pounds.
1.	Without potash and with 357 pounds of basic slag.. ..	1·20	—
2.	With 89 pounds of potash as potash manure salt	4·53	3·33
3.	With 89 pounds of potash as ground felspar	1·69	0·49
4.	With 178 pounds of potash as ground felspar	1·96	0·76

These figures show that this soil responded very well to the application of the soluble potash salts. While it must be admitted that the ground felspar was somewhat available, the effect appears to have been inconsiderable.

It is hard to reconcile such contradictory results as these which are given at length in the preceding pages. The only thing that can be said at the present time is that careful and systematic tests are required in order to determine finally to what extent and under what conditions ground felspar can be economically used in agriculture. The inference to be drawn would seem to be that under certain conditions finely-ground felspar is at least partially decomposed, so that its potash becomes sufficiently available to be made use of by certain crops. Under other conditions we are forced to the conclusion that ground felspar is of little value as a potash fertiliser.

Before proceeding with the description of experiments carried on by the Department of Agriculture it will be necessary to define, as briefly as possible, total and available potash, as the terms are commonly used. Potash is the name given to the oxide of the metallic element potassium. The name is derived from the fact that potash at one time was principally obtained by leaching wood ashes in large iron pots. The letter K is used by chemists as the symbol for potassium, the German name for which is Kalium. The oxide is written K_2O, which signifies that two atomic weights of potassium unite with one atomic weight of oxygen to form potash. Potash as such is a strongly caustic substance which unites with water to form a compound technically known as lye. Fertilisers, both natural and artificial, contain potash, invariably combined with some acid to form a compound or salt, such as sulphate, chloride, carbonate, nitrate, phosphate, or silicate. Although potash (K_2O) does not exist free in a fertiliser, the potassium present in whatever form is figured and reported as total potash (K_2O). Owing to the belief that has always been held by the majority of chemists and agriculturists that the potash combined as it is in the mineral silicates becomes soluble with extreme slowness, if at all, it is customary to distinguish between available and total potash. According to the official methods in vogue in this country the available potash is determined by boiling 10 grms. of the sample with 300 grms. of water thirty minutes, and analysing the water extract. In different places different methods are used; in some cases acid solutions are used to extract with, so that it is difficult to give an exact definition of available potash. However, it may be defined as all the potash that is present, in whatsoever form, which the crop can make use of in

one crop season. The text-book definitions, as well as the State fertiliser laws, are in need of revision in this particular respect. This is especially true in view of the fact that the value of a mixed fertiliser is figured, as far as potash is concerned, on the available or water-soluble potash alone. Even the potash contained in such organic fertilisers as cotton-seed meal and tobacco stems, which undoubtedly becomes available in one season, is not estimated as being available by the present methods of analysis, and therefore in many cases great injustice is done to manufacturers of mixed fertilisers, who should certainly be entitled to all the plant food contained in their mixtures which can be made use of by a crop in a single growing season.

Tobacco is particularly dependent upon abundant supplies of potash. In some of the tobacco-growing districts barnyard and stable manures are used, often enriched with an addition of commercial fertilisers. Since sulphates and muriates of potash are found to be harmful in certain ways to high grades of tobacco, the use of the strongly alkaline potassium carbonate has been largely resorted to on the tobacco crop. Potassium carbonate, which contains about 66 per cent of potash (K_2O), is an expensive compound, costing 90 to 95 dols. per ton, f.o.b. port of entry, or 6 to 7 cents per pound of unit potash. In addition to the cost of this salt, its strong alkalinity is an objectionable feature, and it is a grave question whether the annual addition to the land of a superabundance of such an alkaline salt will not be followed by an actually harmful effect. In view of the successful results which have attended the efforts of the Bureau of Plant Industry to improve the quality and yield of native tobacco by proper selection and breeding, it was decided to make a systematic investigation of the possible use of ground felspar as a potash fertiliser (see *Bull.* 96, Bureau of Plant Industry, U.S. Dept. of Agriculture; "Yearbook Dept. Agr.," 1905, p. 219).

Preliminary to the field and crop experiments which were to follow later, greenhouse experiments were begun early in the winter of 1905-6. Three large beds in the greenhouse, all having the same dimensions ($21\frac{3}{8}$ by $6\frac{3}{4}$ feet by 5 inches), were filled with a common unfertilised meadow soil taken from the surface after the removal of sod and grass roots. Four pounds of ground bone phosphate were broadcasted, and well worked in.

Bed No. 1 now received 2 pounds of potassium carbonate containing about 67 per cent of potash (K_2O). In order that the potassium carbonate might be evenly distributed, it was dissolved in 2 gallons of water, and sprinkled evenly over the bed. After drying out, the earth was again well worked.

Bed No. 2 received 17·4 pounds of finely-ground potter's felspar containing 8·3 per cent of potash (K_2O). This was also broadcasted, and well worked in. It will be seen that Beds 1 and 2 contained nearly equivalent amounts of potash, the only difference being that in one case the soluble carbonate was used and in the other ground rock.

No potash in any form was added to bed No. 3, which was used for comparison. The soil itself, however, contained about 0·5 per cent of total potash, and as the filtered Potomac River water which it was necessary to use for watering throughout the entire experiment contains an amount of potash equal to about 2 parts per million, the tobacco on bed No. 3 did not at any time show the effect of potash starvation.

All three beds were supplied with a sufficient quantity of nitrogen in the form of pure ammonium nitrate. The seed chosen for the experiments was carefully selected Cuban wrapper tobacco. In making experiments of this kind it is necessary to select seedlings as nearly as possible of equal vigour. It is not improbable that many wrong deductions have been drawn from pot or plat experiments in which the need for careful selection of seed has been overlooked.

Tobacco seedlings were set out in four rows of ten plants each in the three beds. The tobacco crop is usually planted with about 8000 plants to the acre, so that the experimental plats represented, as far as plant growth was concerned, one two-hundredth of an acre. The actual amount of potash added to plats Nos. 1 and 2 was equivalent to 280 pounds to the acre. As the original soil contained a sufficient amount of potash to mature some sort of a crop on plat No. 3, it is not possible to state the actual amount of potash present in the three plats. The potash in the soil was not water-soluble, and would not have been termed available in the present sense of the word.

The tobacco grew well throughout the experiment, and for the first six weeks very little difference was noted. After this time, however, it became evident that the plants in plat No. 3 were falling behind. At the end of twelve weeks the plants in plat No. 3 were plainly stunted and much less developed than those in the other two plats. The tobacco grown in plats Nos. 1 and 2 was evenly developed, fully matured, and of a good quality. It was carefully harvested in the usual way, and the yield of green tobacco weighed. After curing, the actual yield of leaf was also recorded. The results, which are shown in the following table, appear to indicate that the felspar potash was available to quite the same extent as that which was added as potasium carbonate :—

TABLE III.—*Results of Greenhouse Experiments with Tobacco Plants.*

No. of Plat.	Source of potash.	Actual weight of green crop.	Estimated weight of green crop per acre.	Actual weight of cured leaf.	Estimated weight of cured leaf per acre.
		Pounds.	Pounds.	Pounds.	Pounds.
1.	Potassium carbonate	154·0	30,800	5·70	1140
2.	Ground felspar ..	155·0	31,000	6·30	1260
3.	—	128·5	25,700	5·30	1060

These yields do not in any case equal those obtained in the field under the best crop conditions, but for a winter greenhouse crop raised in shallow beds they are satisfactory.

On the completion of the greenhouse experiments arrangements were made to carry on field trials in Connecticut and Florida under standard crop conditions. In the tobacco-growing district of Connecticut it is customary to use from 150 to 250 pounds of carbonate of potash to the acre of tobacco. The co-operation of several prominent tobacco-growers was obtained, who each agreed to try an acre, substituting for the usual carbonate 1 ton of potter's spar, running 8·3 per cent of potash, or 186 pounds to the ton. The broadcasting and working in of the felspar was done under the personal supervision of representatives of the Department of Agriculture, and none of the experimental acres received any potash except that contained in the ground spar. All the experimental fields did as well as any in their neighbourhood, and matured excellent crops. The following letters were received from the growers themselves in regard to the use of felspar :—

Tariffville, Con., February 11, 1907.

Dear Sir,—In reply to your letter of February 5, I would say that I used the ton of finely-ground felspar as a potash fertiliser for tobacco, and used no other form of potash on the plat in connection with the felspar. This plat (one-half acre) was treated exactly like the rest of our tobacco lands as regards nitrogen, phosphoric acid, lime, &c.

We had a fine large growth of tobacco where the felspar was used; fully as large as any in our fields, and much larger than in some sections of our fields.

I do not consider this an absolute or hardly a fair test of the felspar, as it was used on land that had previously grown tobacco for several years, and each year we had fertilised heavily with carbonate of potash. I will be pleased to give you more detail if you wish.—Yours respectfully, J. S. DEWEY.

Hartford, Conn., February 7, 1907.

Dear Sir,—In reply to your letter of February 5 regarding the finely-ground spar, would say that we used this material as a potash fertiliser as directed by you last

spring. This was used on comparatively new land, tobacco having been grown only one season previous to this past season. During the growing season we could not see any perceptible difference on the same land between this tobacco and that treated with carbonate of potash, planted side by side. We hung this tobacco in the same shed, it being cut at the same time, where we were able to identify it after it was cured. We are glad to report that the tobacco grown where the ground felspar was used was exceptionally nice tobacco. It was so pronounced by tobacco experts who have examined it.

The tobacco grown on the same character of land beside where this was grown was exceptionally nice tobacco, but we think if there was any preference it would be for that grown on the felspar. It certainly was beautiful in every respect. We should be very glad to conduct an experiment on 1 acre or less on new land that has never grown crops of any kind or been fertilised in any way by stable manure or other fertiliser, and follow this up for, say, three years. We have a piece of land we think well adapted to make the experiment. The result this past year has been so gratifying that we would be very glad to carry it a little further, if possible.

Any further information we can give you we will be glad to furnish.—Yours truly, OLDS and WHIPPLE.

Suffield, Conn., February 16, 1907.

Dear Sir,—Yours received inquiring about the finely-ground felspar sent me. Would say that I used it on 1 acre of tobacco and got very satisfactory growth. The only difference I could detect in tobacco grown on this acre and the adjoining land, where I used cotton-hull ashes for potash, was that the burn of the tobacco grown on the latter was not quite as clear as that of the tobacco grown on the felspar.—Yours respectfully, EDMUND HALLADAY.

Quincy, Fla., March 7, 1907.

Dear Sir,—In reply to your favour, I beg to state that 1 acre of tobacco was grown here last year on ground felspar, and as far as we were able to tell from the appearance of the tobacco in the field the growth was equally as good as where other forms of potash were used. Mr. Underhill, who used this felspar, was not able to harvest the tobacco separately on account of scarcity of labour in harvest season.

I am planting some plat experiments this year in which I have included the ground felspar, to be compared with other forms of potash, and hope to get some information in this way. In addition to this I shall put out at least 2 acres of felspar as a substitute for carbonate of potash, and will report results at the end of the season. —Yours very truly, W. W. COBEY.

Although it is admitted that these experiments have not as yet proved the value of ground felspar for tobacco, it is quite certain that the experimental crops found all the potash they required. If we assume that von Feilitzen and others are right, and that the felspar is of little or no value, we must conclude that the practice of adding potassium carbonate each year to the tobacco fields is unnecessary.

Many attempts have been made by the writer to devise crucial tests which would show decisively whether or not the ground felspar is actually capable of giving up potash to growing plants. One of these experiments, which was undertaken in co-operation with Dr. L. J. Briggs, of the Bureau of Plant Industry, is interesting on account of its direct bearing on this point. A wooden trough of 1 square foot cross-sectional area and 30 feet in length was filled with a poor meadow soil, containing no appreciable quantity of water-soluble potash. About 5 pounds of fine-ground felspar, containing 9·3 per cent of total potash, was then evenly distributed over the surface of the trough, and well worked into the soil. Carbon electrodes of about 1 square foot area were inserted at the extreme ends, and tobacco seedlings set out at 1-foot intervals along the trough. The carbon electrodes were connected to a 110-volt direct-current lighting circuit, and a current of electricity was passed continuously in the same direction through the soil while the growth of the plants was in progress. The amount of current varied with the moisture content of the soil—between the limits of 5 and 15 milli-ampères. The plants made a flourishing growth, and at the end of several weeks it was apparent that the best growth was being made in the neighbourhood of the centre of the trough, the plants at the extreme positive and negative ends being more or less stunted. The soil at the beginning of the experiment was neutral to litmus-paper. At the end of the experiment, when the plants had attained a maximum height of 2 feet, a sample taken from the positive end of the trough reddened litmus-paper, showing it to be decidedly acid. The middle section by the same test was shown to be faintly and the negative end strongly alkaline. While no sweeping deductions can be drawn from the single experiment, it is quite certain that a partial transference of the alkaline bases from the positive to the negative end of the trough had occurred. This effect could only take place with that portion of the bases which had actually passed into solution. The results of this experiment appear sufficiently interesting to warrant repetition under still more careful conditions.

(To be continued).

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

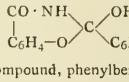
THE following are abstracts of Papers received during the vacation, and published or passed for publication in the *Transactions* :—

162. "*Studies in the Barbituric Acid Series.* I. 1 : 3-*Diphenylbarbituric Acid and some Coloured Derivatives.*" By MARTHA ANNIE WHITELEY. (*Trans.*, 1907, 1330).

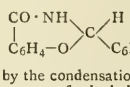
In addition to the coloured derivatives of 1 : 3-diphenylbarbituric acid already described (*Proc.*, 1006, xxii., 200; 1907, xxiii., 180), 1 : 3-*diphenyl*-5-*diphenylmethyleuebarbituric acid*, $CO<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}CPh_2$, was prepared from 1 : 3-diphenylbarbituric acid and benzophenone dichloride; it forms yellow prisms melting at 264°, and, like the similarly constituted benzylidene derivative, yields a colourless acid, 1 : 3-*diphenyl*-5-*diphenylmethylbarbituric acid*, $CO<^{NPh\cdot CO}_{NPh\cdot CO}>CH\cdot CHPh_2$, m. p. 205—206°, on reduction.

163. "*Phenylbenzometoxazone and Related Derivatives.*" By ARTHUR WALSH TITHERLEY. (*Trans.*, 1907, 1419).

According to McConnan and Titherley (*Trans.*, 1906, lxxxix., 1318), O- and N-acylsalicylamides are labile and mutually transformable through an intermediate cyclic metoxazone structure. The alternative tautomeric formula for N-benzoylsalicylamide is—



and the related compound, phenylbenzometoxazone,—



has been isolated by the condensation of salicylamide and benzaldehyde by means of alcoholic hydrogen chloride (compare Keane and Nicholls, *Trans.*, 1907, xci., 266). The relation between phenylbenzometoxazone and N-benzoylsalicylamide is confirmed by the fact that the former passes into the latter on careful oxidation. When salicylamide and benzaldehyde condense in presence of

anhydrous sodium acetate, benzylidenesalicylamide results as well as phenylbenzometoxazone :—

$$C_6H_4\!<\!\begin{matrix}CO\cdot NH_2\\OH\end{matrix} + C_6H_5\cdot CHO \rightarrow \rightarrow C_6H_4\!<\!\begin{matrix}CO\cdot N{:}CH\cdot C_6H_5\\O\end{matrix}.$$

An isomeric benzylidenesalicylamide has also been obtained by rearrangement of phenylbenzometoxazone with pyridine and alkali. The two isomerides are amorphous and similar in physical properties, but differ markedly in stability ; that produced by condensation is stable, but the other, derived from phenylbenzometazone, rearranges completely into this compound on melting. The two benzylidenesalicylamides are probably geometrical isomerides :—

$OH\cdot C_6H_4\cdot CO\cdot N$ $\Vert$ $H\cdot C\cdot C_6H_5$	$OH\cdot C_6H_4\cdot CO\cdot N$ $\Vert$ $C_6H_5\cdot C\cdot H$
syn- (Labile) Benzylidenesalicylamide.	*anti*- (Stable) Benzylidenesalicylamide.

The production of phenylbenzometoxazone in the condensation of benzaldehyde and salicylamide evidently takes place through the rearrangement of *syn*-benzylidenesalicylamide first formed, so that the mechanism in presence of sodium acetate may be represented :—

$$C_6H_5\cdot CHO + C_6H_4\!<\!\begin{matrix}CO\cdot NH_2\\OH\end{matrix} \rightarrow \begin{matrix}OH\cdot C_6H_4\cdot CO\cdot N\\ \Vert \\ C_6H_5\cdot C\cdot H\end{matrix} \rightarrow \begin{matrix}OH\cdot C_6H_4\cdot CO\cdot N\\ \Vert \\ H\cdot C\cdot C_6H_5\end{matrix} \rightarrow \begin{matrix}C_6H_4\cdot CO\cdot NH\\ | \\ O\!-\!\!-\!\!-\!\!-\!CH\cdot C_6H_5\end{matrix}.$$

The reversible relation which exists between the *syn*-open-chain formula and the ring (metoxazone) affords striking confirmation of McConnan and Titherley's theory (*loc. cit.*) of cyclic metoxazone tautomerism as applied to the acylsalicylamide group.

Amorphous syn-*benzylidenesalicylamide* on boiling with alcohol or acetic acid becomes crystalline and them melts at 182°. In acetone solution it gives a violet ferric chloride reaction. anti-*Benzylidenesalicylamide*, which has not been obtained crystalline, gives a similar reaction. Both yield *sodium* salts and *benzoyl* derivatives.

164. "*The Application of Baeyer's Reduction to Benzoin and its Derivatives.*" By James Colquhoun Irvine and John Weir. (*Trans.*, 1907, 1384).

Baeyer's method of reduction has been applied to benzoin and to a number of its derivatives. In every case, stilbene was obtained as the final product, irrespective of the nature of the side-chains present in the compound reduced. As in previous reductions of a similar nature, it has been shown that the reactions proceeded through the intermediate formation of deoxybenzoin. The reduction of benzoin to either stilbene or deoxybenzoin can be so readily controlled that the process can be used as a method of preparing these compounds, the yield being in each case about 60 per cent of the theoretical amount.

In preparing benzoin methyl ether by Fischer's process (*Ber.*, 1893, xxvi., 2412), two compounds were isolated which appear to be products of complicated side-reactions. One of these substances, which melted at 185°, is a condensation compound produced by the union of a molecule of benzoin with one of benzoin methyl ether with loss of water. The other compound (m. p. 285°) is regarded as a tetramethylene derivative produced by the union of two molecules of benzoin methyl ether. The mode of its formation resembles that of the benzoin condensation, and seems to depend on the action of nitriles present as impurities in the benzoin used.

165. "*Aromatic Azoimides.* Part II. *Ortho- and Meta-hydroxyphenylazoimides.*" By Martin Onslow Forster and Hans Eduard Fierz. (*Trans.*, 1907, 1350).

o-*Hydroxyphenylazoimide*, $HO\cdot C_6H_4\cdot N_3$, prepared by the action of hydroxylamine on diazotised *o*-aminophenol, crystallises in colourless needles containing $\frac{1}{2}H_2O$; it quickly becomes brown when exposed to light, darkens at 120—130°, and detonates vigorously at 140—145°. The *sodium* derivative is colourless, and does not change into a blue variety corresponding to the blue potassium derivative of *p*-hydroxyphenylazoimide. The *benzoyl*, *p-nitrobenzoyl*, and *p-toluenesulphonic* derivatives melt at 45°, 101°, and 72° respectively.

m-*Hydroxyphenylazoimide*, produced from diazotised *m*-aminophenol and either hydroxylamine or hydrazoic acid, crystallises from petroleum in colourless needles which melt at 36·5°, and quickly become brown when exposed to light ; the *benzoyl* and *p-nitrobenzoyl* derivatives melt at 50° and 136° respectively.

166. "*The Influence of Mercuric Iodide on the Formation of Sulphonium Iodides.*" By Thomas Percy Hilditch and Samuel Smiles. (*Trans.*, 1907, 1394).

Many sulphonium bases are difficult to obtain by the usual method, namely, the addition of alkyl halide to sulphide, owing to the secondary action of the alkyl halide with the sulphonium salt as the latter is formed, and the authors have shown that ethyl disulphide and ethyl iodide, at the ordinary temperature, furnish triethylsulphonium iodide. Such instances as this are usually found where the initial addition of alkyl iodide proceeds slowly. The formation of sulphonium bases, however, is greatly accelerated if the reaction is carried out in presence of mercuric iodide ; and in this way, the sulphonium salt can be isolated before the secondary action of the alkyl halide has set in. Thus, ethyl disulphide and ethyl iodide in presence of mercuric iodide yield diethylthioethylsulphonium, $(C_2H_5)_3S_2I,2HgI_2$, and dibenzyl sulphide with methyl or ethyl iodide and mercuric iodide furnishes the compounds $(C_7H_7)_2(CH_3)SI,HgI_2$ and $(C_7H_7)_2(C_2H_5)SI,HgI_2$.

167. "*Benzoflavol* (2 : 8-*Dihydroxy-5-phenyl-3* : 7-*dimethylacridine*)." By Albert Ernest Dunstan and Louisa Cleaverley. (*Trans.*, 1907, 1619).

Following the method laid down by Dunstan and Hewitt (*Trans.*, 1906, lxxxix., 1472), the authors have prepared 2 : 8 - *dihydroxy-5-phenyl* - 3 : 7 - *dimethylacridine* (*benzoflavol*) from benzoflavine. The *sulphate*, *dichromate*, *platinichloride*, and *picrate* were described.

On benzoylation, benzoflavol yields a *dibenzoyl* derivative, and on acetylation a *diacetyl* derivative, m. p. 239—242°. The latter, on methylation and subsequent hydrolysis, furnishes the *anhydro* - *base*,

$$HO\cdot C_6H_2Me\!<\!\begin{matrix}NMe\\CPh\end{matrix}\!>\!C_6H_2Me{:}O.$$

168. "*The Action of Bromine on 5-Phenylacridine and its Halogen Derivatives.*" By Albert Ernest Dunstan and Thomas Percy Hilditch. (*Trans.*, 1907, 1659).

The following compounds have been prepared and submitted to the action of bromine :—(1) 5-*p*-Chlorophenylacridine ; (2) 5-*p*-bromophenylacridine ; (3) 5-phenylacridine ; (4) monobromophenylacridine. The resulting compounds have been methylated either by methyl iodide or dimethyl sulphate. Substances 1 and 2 gave dibromo-derivatives which lost bromine on treatment with dimethyl sulphate. Substance 3 gave a tribromophenylacridine which, with dimethyl sulphate, also lost bromine. Substance 4 was normally methylated. The authors conclude that these bromine derivatives are additive (compare Senier and Austin, *Trans.*, 1904, lxxxv., 1196), the added atoms occupying the para-meso-positions.

169. "*The Relation between Viscosity and Chemical Constitution.* Part I. *The Viscosity of Pyridine Solutions.*" By Albert Ernest Dunstan, Ferdinand Bernard Theodore Thole, and John Samuel Hunt. (*Trans.*, 1907, 1728).

The authors have applied the methods and results of

Dunstan (*Trans.*, 1904, lxxxv., 817; 1905, lxxxvii., 11; 1907, xci., 83) to solutions of pyridine, α- and β-picoline, and 2:6-lutidine in various solvents. These bases in aqueous solution give curves which exhibit maxima, the discontinuities being at points of simple molecular concentration. These maxima are attributed to the addition of the elements of water at the nitrogen atom of the pyridine, or its homologues.

170. "*The Atomic Volumes of Phosphorus.*" By Edmund Brydges Rudhall Prideaux. (*Trans.*, 1907, 1711).

The author has determined the coefficients of expansion of phosphorus and phosphorus pentachloride, and has calculated the values of the constants from the equations $V_t = V_0(1+at+\beta t^2)$, expressing the expansion of phosphorus between 60° and 235°, and $V_t = V_0(1+at)$, expressing the expansion of phosphorus pentachloride between 160° and 190°. From these equations, values are obtained for the specific volumes of phosphorus and phosphorus pentachloride at their respective boiling-points.

The atomic volume of quinquivalent phosphorus can thus be compared with those of tervalent and elementary phorphorus.

171. "*The Action of Potassium Sulphite on Potassium Tetrathionate in Aqueous Solution.*" By Arthur Colefax.

By the joint estimation of the iodine titration and the acidity developed in the solution when the iodine titration is completed, the nature of the interaction of potassium sulphite and tetrathionate in aqueous solution has been investigated.

If potassium sulphite and tetrathionate react in equimolecular proportions in aqueous solution, the conversion of sulphite into thiosulphate and consequent formation of trithionate which occurs does not proceed to completion, and pentathionate is not permanently formed in the solution. If the relative proportions in which these bodies are originally present in the solution are either $K_2SO_3 : \frac{1}{2}K_2S_3O_6$, or $K_2SO_3 : 2K_2S_4O_6$, the theoretically complete conversion of sulphite into thiosulphate takes place. In the latter case, where the proportions are $K_2SO_3 : 2K_2S_4O_6$ when the sulphite has been completely converted into thiosulphate, pentathionate is found in the solution in considerable amount.

Certain preliminary experiments established that—(*a*) Potassium sulphite and trithionate do not react in aqueous solution; (*b*) potassium thiosulphate and tetrathionate react in aqueous solution to form pentathionate, the resulting sulphite being immediately re-converted into thiosulphate; (*c*) potassium thiosulphate and trithionate react in aqueous solution, although to an extremely small extent; and (*d*) potassium sulphite rapidly abstracts sulphur from pentathionate when the two salts react in aqueous solution.

172. "*The Adsorption of Iodine by Carbon.*" By Oliver Charles Minty Davis. (*Trans.*, 1907, 1666.)

An investigation has been carried out on the adsorption of iodine dissolved in various organic solvents, by means of animal, sugar, and cocoanut charcoal.

The main objects of the research were to investigate the effect of temperature and time on the amount of adsorption, and to compare the adsorbing values of the three forms of carbon.

The effect of temperature was found to be very small, but that of time was well marked.

The experiments demonstrate the fact that adsorption, although rapid at first, proceeds slowly for lengthened periods after a "surface equilibrium" has been maintained, proving that both surface action and diffusion are concerned in the mechanism of adsorption.

The adsorbing values of animal and sugar carbon are roughly the same, whilst that of cocoanut carbon is much less than these.

173. *Adsorption Formulæ.*" By James William McBain. (*Trans.*, 1907, 1683.)

The results of recent work on absorption have been expressed by either of the following two formulæ, which are applicable to gases or solutions:—

$$\frac{x}{m} = \beta c^{1/p} = \beta\left(\frac{a-x}{v}\right)^{1/p} \quad \text{I.}$$

$$\lambda = \frac{v}{m} ln \frac{a}{a-x} = \alpha\left(\frac{a}{v}\right)^{-1/n} \quad \text{II.}$$

where x is the amount of substance adsorbed, a is the total amount of that substance, $\frac{a-x}{v} = c$ its concentration in the fluid phase, m the weight of adsorbing substance, and λ, β, α, p, and n are constants.

There are, however, some very serious disadvantages inherent in the use of the λ-formula, whereby an equilibrium is referred to a parameter a/v with which it has no apparent connection. This expression, introduced to represent the amount of adsorption, does not lead to any definite number characteristic of each set of substances, and, moreover, its results are irreconcilable with each other and with experiment.

174. "*The Diazo-derivatives of Benzenesulphonylbenzidine.*" By Gilbert T. Morgan and James Morton Hird. (*Trans.*, 1907, 1505.)

Benzenesulphonylbenzidine and as-*benzenesulphonylmethylbenzidine*, $C_6H_5{\cdot}SO_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}C_6CH_4{\cdot}NH_2$, give rise to stable, coloured diazonium salts; those derived from the latter base are of interest in connection with the formulæ recently put forward for diazonium derivatives, because they show that the presence of a labile hydrogen atom is not necessary for the development of colour in this series of substances.

175. "*The Interactions of Aromatic Amines and Para-diazoimides.*" By Gilbert T. Morgan and Frances M. G. Micklethwait. (*Trans.*, 1907, 1512.)

The para-diazoimides recently described by the authors combine additively with the more reactive aromatic amines to give rise to aminoazo-compounds.

This combination occurs in some instances when the reagents are intimately mixed in the dry state, the reaction being accelerated by the addition of a small amount of pyridine. Benzenesulphonyl-*p*-phenylenediazoimide combines in this way with α- and β-napthylamines and certain of their derivatives, but the reaction does not take place with aniline and its homologues.

176. "*Molecular Aggregation in Solution as Exemplified in Aqueous Mixtures of Sulphuric Acid with Inorganic Sulphates.*" By John Holmes and Philip John Sageman. (*Trans.*, 1907, 1606.)

The authors have determined the volumetric data of a series of mixtures of dilute sulphuric acid with aqueous solutions of neutral inorganic sulphates. In all cases, the volume of the mixture was found to be greater than the sum of the initial volumes.

From a consideration of the results obtained, the authors conclude that the volumetric changes are due to physical forces inherent to the molecules, and this theory is supported by a comparison with the results obtained in mixtures in which chemical change is known to occur.

By elimination of extraneous influences due to the solution medium, the relative aggregations of the interacting molecules can be determined.

177. *The Wandering of Bromine in the Chlorination of Bromoanilines.*" By Walter William Reed and Kennedy Joseph Previté Orton. (*Trans.*, 1907, 1543.)

When *p*-bromoaniline is directly chlorinated, the normal product, 2:6-dichloro-4-bromoaniline, is not alone formed. Partial displacement of the bromine by the chlorine takes place, and a mixture of chlorodibromo-, dichlorobromo-, and *s*-trichloro-anilines results, which cannot be resolved into its constituents. Such a reaction does not occur only when excess of chlorine is used, but also with the calculated quantity of the reagent. The solvent has little effect, the same mixture being obtained when 20 per cent

hydrochloric acid or such anhydrous solvents as benzene, chloroform, or carbon tetrachloride are employed. Similar results were observed on treatment of 2 : 4-dibromoaniline with one molecular proportion of chlorine, *s* tribromoaniline being among the products of the change. *o*-Bromo-, *m*-bromo-, and 2 : 6-dibromo-aniline, on the other hand, yield respectively only a single chlorinated product.

2 : 6-Dichorobromoaniline can be obtained indirectly by two methods, either by molecular rearrangement of acetyl-chloroamino-2-chloro-4-bromobenzene which yields the acetyl derivative of the aniline, or by the action of acetyl-chloroamino-2 : 4-dichlorobenzene on *p*-bromoaniline, when 2 : 4-dichloroacetanilide and 2 : 6-dichloro-4-bromoaniline are formed :—

$$C_6H_4Br{\cdot}NH_2 + 2C_6H_3Cl_2{\cdot}NClAc = C_6H_2Cl_2Br{\cdot}NH_2 + 2C_6H_3Cl_2{\cdot}NHAc.$$

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, October 25th, 1907.

Prof. J. PERRY, F.R.S., President, in the Chair.

A PAPER by Dr. J. A. FLEMING, F.R.S. on "*Magnetic Oscillators as Radiators in Wireless Telegraphy*," was read by the author.

An open or Hertzian oscillator is called an electric oscillator because the effects produced in space are due in part to the potential of the free charges at the ends. A closed circuit oscillator is called a magnetic oscillator because the effects it produces are wholly due to current. Hertz showed that the energy radiated per period from an open oscillator could be expressed by the formula $E = 16\pi^4\phi^2/3\lambda^3$, where λ is the wave-length and ϕ the electric moment. The author has shown that a similar formula $E = 16\pi^4 M^2/3\lambda^4$, where M is the magnetic moment, holds good for the closed circuit oscillator. Assuming persistent or undamped oscillations to be used, these formulæ were transformed by the author into two others, viz. :—$W = 87 \times 10^{-29} l^2 a^2 N^2$ for the open oscillator, and $W = 4 \times 10^{-38} S^2 a^2 N^4$ for the closed oscillator, where *a* is the R.M.S. value of the current in the oscillator and N is the frequency. Hence the radiation from the open oscillator varies as the square of the frequency, and that from the closed one as the fourth power. The paper describes experiments made with flat square coils of various sizes used as magnetic oscillators in the quadrangle of University College, London. In one circuit undamped oscillation were set up by means of a Poulsen arc, and the induced oscillations created in the other circuit at a distance were detected and measured by means of the author's oscillation valve or glow-lamp detector. The distance separating the two circuits was varied from about 50 to 250 feet. Curves were obtained showing how the secondary current varied with the distance of the circuits apart and with their relative position. It was shown that the inductive effect was greatest when the flat coils were in a horizontal position and at a certain distance above the earth.

The law of variation with distance proved to be something between the inverse cube and the inverse square of the distance. It was then shown that increase in size of the coils had a very marked action in increasing the inductive effect, and also that for equal power the use of the spark method creating intermittent oscillations in the primary gave better effects than the use of the arc or undamped oscillations.

It was also shown that for the coils used the true radiation of energy was very small, and therefore that the distance effects obtained were almost entirely due to magnetic or faradaic induction.

Suggestions were then made for increasing the efficacy of the ordinary inductive type of wireless telegraphy by the use of high frequency oscillations in the primary circuit, and a suitable detector such as the author's oscillation valve combined with a telephone as a receiver in the secondary circuit. Such a method would have a far greater reach than the ordinary low-frequency alternating current inductive telegraphy and not be open to the objection of disturbing commercial telephonic circuits.

Mr. A. RUSSELL thanked the author for his clear exposition of the theory of electric oscillators and for the valuable formulæ he gave for magnetic oscillators. The experiments described were exceedingly interesting and instructive. It was, however, difficult to interpret some of the results obtained. He asked whether the author had been able to find a position for the secondary coil in which no current was induced in it. Possibly buried pipes or metallic conductors, iron girders in adjacent buildings, or iron railings in the neighbourhood, might have had some influence in modifying the inductive effects between the coils.

Mr. TAYLOR said that the Post Office had tried arrangements similar to those described for magnetic space telegraphy, and had found that the closed circuit method was inferior to that in which earth-connected vertical coils were used. The ratio between the received currents when using an earth-connected and a closed circuit was often as great as eighty to one, and he thought the improvements in the closed-circuit method would have to be very great to make it equivalent to the earthed-circuit method.

A paper "*On the Use of Variable Mutual Inductances*" was read by Mr. A. CAMPBELL.

In connection with wireless telegraphy the measurement of small inductancss and capacities is of importance ; one of the methods described has special reference to small self-inductances. Mutual inductances can be more easily dealt with than self-inductances, for the former can be (1) more accurately calculated from dimensions, (2) are less affected by change of frequency, and (3) when variable can be made to pass through zero value. A convenient form of variable mutual inductance consists of a continuously variable part and a series of steps. The first consists of two equal parallel coils with a third coil moving parallel to their planes round an axis eccentric to the fixed coils. The scale thus obtained is very open near zero (which is an advantage) and the graduation is done by experiment, a theoretical discussion being given in an appendix. The steps are obtained by means of another fixed coil of stranded wire, each strand giving an equal subdivision. The model shown had two ranges, from 0·01 up to 200 and 2000 microhenries. A variable mutual inductance of this type has a number of applications. It is obviously convenient for calibrating ballistic galvanometers. By means of it mutual inductances of all values can be readily measured. By several methods it can be used to measure capacities, and the formulæ required are mostly very simple. Its most important application, however, appears to be to the measurement of small self-inductances as follows :—Let the variable mutual inductance be called W. With a source of intermittent or alternating current and any convenient detector (vibration galvanometer, telephone, &c.) a bridge with corners A, B, C, D is formed, in which BD and DC are equal non-inductive arms, AB is the fixed secondary of W, and AC has resistance and self-inductance equal to those in AB. The detector is across BD, while the source is applied at D and also through the primary of W connected to A. When W is set to zero reading a balance is obtained. An unknown small self-inductance N is now inserted in AC, and the balance restored by adding resistance in AB and adjusting the mutual inductance W. The reading of W when doubled gives directly the value of the unknown N. The method is really a differential one and can also be used to give very accurate measurements of the difference between two nearly equal large self-inductances.

The discussion on Mr. Campbell's paper was postponed until the next meeting.

NOTICES OF BOOKS.

A Scheme for the Detection of the more Common Classes of Carbon Compounds. By FRANK E. WESTON, B.Sc. (Lond.), F.C.S. New Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

THE second edition of this book has been considerably enlarged, and its size is now almost twice that of the first edition, issued three years ago. The new matter, which accounts for this extra bulk, is of considerable importance, and although the beginner will now find that there is much which is beyond his requirements, the usefulness of the book for Honours students is considerably increased. The greater part of the additional matter deals with the identification of individual members of groups, and when the student has discovered, for instance, that the substance he has to identify is a phenol, he will no longer have to look up in his text-book the information which will enable him to decide what particular phenol it is—he will find full enough details of the chemical and physical properties of the more common members of the class to proceed to the identification of the individual. Fuller information is also given with regard to the experimental arrangement of some of the tests, and several new methods, which have been perfected since the appearance of the first edition, are now included. The book will be found a valuable aid in systematising the students' practical work in organic chemistry, and giving him a grasp of the chief reactions of all the more important classes of carbon compounds, and is specially suitable for the use of candidates for the London B.Sc. and the Honours Chemistry Examination of the Board of Education.

Fire Tests with Petrol Tanks. (Henze Patents). London: The British Fire Prevention Committee. 1907.

THE results of fire tests with tanks containing petrol and other inflammable liquids, and fitted with patent safety devices, are described in this pamphlet. The special appliances employed include a safety plug, and an interior safety wire-gauze tube, the patents of which have recently been acquired by the Safety Non-Explosive Reservoir Company, Ltd. The tanks and vessels were subjected to severe tests in order to prove the efficiency of the devices, and the results appear to show that the inventions are of great value as a safeguard against explosion. The safety plug prevents the bursting of the vessels, even when a bonfire is lit beneath them, the escaping vapour merely burning quietly at the mouth, and if the safety gauze tube is fitted into the interior there appears to be practically no danger of the vapour igniting inside the vessel.

E. Merck's Annual Reports. Vol. XX. Darmstadt: E. Merck. 1907.

THIS volume of annual reports gives a brief review of all the novelties which have come into use in therapeutics during the last twelve months. Statistics concerning the doses and use of new drugs are given, and notes upon the results obtained with them, and also upon the adoption of well-known preparations in diseases for which they have not hitherto been recommended. A bibliographical index gives a list of publications upon therapeutical and pharmaceutical subjects which appeared in 1906, and a table is added showing the approximate prices of all the preparations mentioned in the reports. The book will be sent free to medical men and others interested in pharmacology and therapeutics, on application to the London office at 16, Jewry Street, E.C.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Sir R. J. Collie, Sir Murland Evans, Bart., and Mr. H. Richardson were elected Members.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 16, October 14, 1907.

Analysis of Mixtures of Air and Combustible Gases and Vapours.—Jean Meunier.—With ordinary measuring cylinders of fixed volume the proportions of the mixtures used can only be multiples of the volume given by the pipette, and it is impossible to weigh the gas for analysis. The author's improved apparatus for the purpose consists of a measuring cylinder graduated in cubic centimetres and closed at the bottom by a movable copper piston on which some mercury is poured. The upper end of the cylinder is somewhat constricted, and can be closed by a glass cap with a cock through which the gases to be investigated can be introduced. A known weight of volatile liquid is put into the measuring cylinder by means of a pipette, and by adjusting the piston a given weight of gas can be made to occupy any desired volume.

A New Method of Rapidly Determining Methane.—Nestor Gréhant.—The author finds that, when an electric current passes along a red-hot platinum wire in mixtures of air and methane, incomplete combustion is produced unless the current is passed from two hundred to four hundred times, or even more. The figures he has obtained show, moreover, that, in his eudiometer, methane can be estimated rapidly and with a sufficient degree of accuracy for most practical purposes.

Vinylic Alcohol of the Type ArR=C=CHOH.—MM. Tiffeneau and Daufresne.—No secondary vinylic alcohol has yet been isolated, and it has hitherto generally been believed that vinylic alcohols are incapable of existing in the free state. When, however, dry potassium acetate in alcoholic solution and alcoholic potash are allowed to act in succession upon the dibromide of $OCH_3-C_6H_4-CH_2-CH_2-CH_3$, the following reaction takes place:—

$$OCH_3-C_6H_4-CH_2-CHBr-CH_2Br \rightarrow OCH_3-C_6H_4-C\equiv\begin{matrix}CHOH\\CH_3\end{matrix}.$$

The product, formerly supposed to be anisylcyclopropanol, has now been shown by the authors to be a true vinylic alcohol, methylanisyl ethanol. It is stable in neutral or alkaline media, and is the first representative of the class which has been prepared.

Reactions of Nickel-plating Bath.—A. Brochet.—The deposition of nickel must be carried out in a neutral bath; in a slightly acid solution gas is evolved and the metal rises in the form of scales. In presence of sulphates sulphuric acid is set free and oxygen evolved. The presence of alkaline salts is essential in order that nickel may be satisfactorily deposited; ammonium salts are the best to employ. They give with nickel sulphate complex salts which dissociate into cations, NH_4, and anions, $(SO_4)_2Ni$, and these latter have their charge neutralised by that of the Ni ions furnished by the anode. Nickel sulphate is formed and also oxygen and sulphuric acid. Nickel peroxide also results, owing to the intermediate formation of unstable nickelic sulphate. These reactions are not modified by the addition of chlorides; a precipitate of hydrate of nickel oxide is formed and is deposited at the same time as the nickel. In order to prevent the bath becoming acid it is best to add salts which do not easily dissociate, and also to add boric acid in order to make the deposit white.

THE CHEMICAL NEWS.

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VULCANISATION TESTS WITH PLANTATION RUBBER.

(Third Communication).

By CLAYTON BEADLE and HENRY P. STEVENS.

Specific Gravity of Vulcanised but Unloaded Rubbers.

In previous communications to the Chemical News (vol. xcvi., pp. 37 and 187) we have described the results of a number of vulcanisation tests on high-grade plantation rubbers and also on hard-cure para. The vulcanisations were carried out in our laboratories on mixings consisting of caoutchouc and sulphur only, the proportion of the latter being usually 6 per cent, although mixings were also vulcanised containing 5 per cent and 8 per cent of sulphur. The vulcanised samples were then tested and the tensile strength and elongation recorded.

With a view to carrying our investigations a step further, we have determined the apparent specific gravity of the vulcanised samples and subjected our figures to a close examination, with a view to finding some relation between the specific gravity and conditions under which the samples were vulcanised, it such should exist.

In a great number of cases, owing to the simultaneous variation both in temperature (or pressure) and time of vulcanisation, it is not possible to make a direct comparison, although in some of these cases the tensile strength and elongation affords some clue. Unfortunately, the specific gravity of many samples was not taken till many months after they had been prepared, and the results are vitiated by the tendency of the specific gravity to increase on keeping, especially in the case of fully cured samples.

In this respect, the over-cured samples which had been kept many months showed comparatively high specific gravities, and a loss in tensile strength was generally accompanied with a marked increase in specific gravity, and both plantation rubbers and hard-cure para showed substantially the same behaviour.

Turning now to the recently vulcanised samples, the following figures illustrate the variation in specific gravity with the cure.

Mixing D_3 consisted of hard-cure para with 6 per cent of sulphur; O_3, a plantation rubber (block) with 8 per cent of sulphur; and V_2, another plantation rubber (biscuit) with 6 per cent of sulphur.

Table III.

	Length of cure (hours).	Apparent specific gravity.
D_3 270	3	0·9489
D_3 266	4	0·9565
D_3 260	5	0·9582
D_3 257	6	0·9566
O_3 297	2	0·9517
O_3 299	2½	0·9534
O_3 295	2½	0·9567
V_2 271	3	0·9579
V_2 264	4	0·9560
V_2 258	5	0·9564
V_2 255	6	0·9462

In many cases the specific gravities of a series of cures made on one mixing give figures differing but little from one another.

Mixing O_2 consisted of plantation rubber (block); Q_2, hard-cure para; P_2, hard-cure para; and R_2, plantation rubber (biscuit). All with 6 per cent of sulphur.

Table IV.

	O_2.	P_2.	Q_2.	R_2.
	0·9429	0·9464	0·9554	0·9412
	0·9494	0·9387	0·9454	0·9492
	0·9429	0·9450	0·9456	0·9496
	0·9474	0·9459	0·9476	0·9484
	0·9474	0·9444	0·9522	0·9474
	0·9454	—	0·9530	—
	0·9449	—	0·9472	—
	0·9479	—	—	—
Mean	0·9460	0·9414	0·9495	0·9471

In spite of the fact that many of these were under-cured and some over-cured, the specific gravities, taken a few weeks after they were made, revealed the fact that the differences are very small. Moreover, it is noteworthy that two totally different types of plantation rubber, as block and biscuit, one from Malay and the other from Ceylon, and hard-cure para from the Amazon, all three prepared in different ways, gave results practically identical with one another.

A very large number of specific gravity determinations have been made, but no object would be gained by giving them in detail, as they would not serve any useful purpose. As a general rule, the specific gravity does not fall below 0·94 and seldom reaches 0·96, except in samples which have been over-cured and kept some months, when they usually exceed 0·96 or even reach 0·98 in samples containing 6 per cent of sulphur.

Portions of the vulcanised samples which had been used for determination of tensile strength, and which had been put aside for a short time gave the same figures for specific gravity as pieces of the same sample which had not been subjected to distortion. On the other hand, it examined immediately after testing, the sample showed a lower specific gravity than an untreated portion of the same sample.

Tests with Ceylon Biscuit Rubber.

In extending our researches on vulcanising rubber in other directions, we have made up a few mixings and carried out a number of vulcanisation tests with Ceylon biscuit rubber. This biscuit was the best obtainable, and on analysis showed a very high percentage of caoutchouc.

Table V.—*Ceylon Biscuit.*

Moisture	0·5
Albumenoids	0·1
Resin	2·8
Ash	0·4
Caoutchouc (by difference)	96·2

The results of the tests are given in Table VI.

Table VI.

Vulcanisation reference number.		Tensile strength, in grms.	Elongation at rupture when original = 1·0.	Elongation under a strain 1500 grms. when original = 1·0.
212		548	6·9	—
217		1720	13·0	12·4
215	R_2	2352	13·6	13·0
226		2634	13·4	10·8
223		2331	11·4	8·9
231		2280	14·7	12·9
249		2436	13·5	12·5
234		2513	14·5	11·7
271	V_2	1472	12·0	11·3 (*a*)
264		2639	13·0	10·1 (*b*)
258		2645	13·0	9·8 (*c*)
255		Very short and weak.		(*d*)

Duration of vulcanisation: (*a*) Three hours, (*b*) four hours, (*c*) five hours, (*d*) six hours.

As far as possible the vulcanisations are arranged in order of duration and temperature, starting with the shortest and ending with the longest cure. In the case, however, of vulcanisations V_2 271, 264, 258, 255 a close comparison is possible, as the temperature of vulcanising was in all cases the same. V_2 271 is obviously undercured; it shows an elongation of 11·3 under a load of 1500 grms. On giving this mixing four hours' treatment instead of three, the tensile strength rises practically to the maximum, the elongation being reduced from 11·3 to 10·1. On giving the mixing still another hour's vulcanisation the tensile strength is not materially increased, while the elongation is reduced to 9·8. On vulcanising for six hours a very short and brittle product was obtained, which was so weak that it did not appear worth while to test it. V_2 255 is therefore considerably over-vulcanised, and V_2 258 is also probably vulcanised longer than is needful.

As we are only able to record the results of vulcanisation tests on two mixings with Ceylon biscuit, we should hesitate to draw too positive a conclusion from the results of our tests. On the whole, the tensile strengths, when averaged up, are not very different from the figure obtained in the case of hard-cure para, and there is not much to choose between them. On the other hand, taken in conjunction with the tests on vulcanised block rubber published in our previous communication, it is obvious that the samples of block we have examined yield a vulcanised product of greater tensile strength than the sample of Ceylon biscuit.

While not desiring to push this conclusion too far, we must admit that the tests with Ceylon biscuit were made on samples from one plantation only; yet it is not likely that other samples of biscuit would yield better results, as we chose for purposes of our experiments one of the highest quality biscuit to be found on the market.

THE COMBUSTION OF SULPHUR IN AIR AND OXYGEN.

By J. H. KASTLE and J. S. McHARGUE.

SULPHUR dioxide has long been employed as a disinfectant and germicide. For many purposes it is regarded as highly efficient and in general its mode of action is sufficiently well understood. Like other substances employed for purposes of disinfection its efficiency is dependent on various conditions such as temperature, moisture, &c., and to some of these its relation is still not well understood. An experimental study of its mode of action as a germicide has therefore been recently undertaken in the Hygienic Laboratory of the U.S. Public Health and Marine Hospital Service, and the observations herein described were made in connection with this investigation. Ordinarily, the sulphur dioxide required for disinfection is obtained by burning sulphur in air in pots or furnaces, the latter specially designed for this purpose. It therefore became a matter of interest in this connection to determine whether sulphur dioxide is the sole product of the combustion of sulphur, and especially to determine whether any sulphur trioxide is formed during the combustion.

According to Hempel (*Ber.*, xxiii., 1455), when sulphur is burned in oxygen the quantity of sulphur trioxide produced increases with increase in the pressure of the oxygen to 40 to 50 atmospheres, when approximately half of the sulphur is converted into the trioxide. At still higher pressures the quantity of sulphur trioxide formed is less than this, and at atmospheric pressure the gas resulting from the combustion of sulphur contains 2 per cent of sulphur trioxide and 98 per cent of sulphur dioxide.

According to Hempel, in order to determine the several amounts of these two substances in the gases resulting from the combustion of sulphur, the outlet tube of the autoclave was opened and the sulphur dioxide absorbed by drawing the gases through an absorption flask containing iodine solution. In order to effect the most complete separation of the sulphur dioxide from the trioxide, the autoclave was placed in hot water. The sulphur dioxide produced was determined by titration of the iodine solution and the sulphuric acid remaining in the autoclave was determined gravimetrically. According to this author, an exact agreement of the results could not be obtained.

Theoretically, at least, it would seem possible to determine the quantities of sulphur dioxide and trioxide in a mixture of gas by determining (1) the quantity of sulphur dioxide by means of decinormal iodine, and (2) the sulphur trioxide by a gravimetric determination of the total sulphur in the solution after absorption. In order, however, that these methods may be employed to advantage in the actual study of sulphur-dioxide disinfection it is essential that they be rapid and easy of execution. The attempt was made therefore to determine both the sulphur dioxide and trioxide volumetrically. This we have been able to accomplish in two ways:—(1) By passing the gases resulting from the combustion of the sulphur through a solution of decinormal iodine. In such a solution the sulphur dioxide is absorbed by conversion into sulphuric acid and any sulphur trioxide present in the gas is absorbed by the water which is present. In our earlier work on this subject the iodine solution contained in the several absorption flasks was poured into a measuring flask of convenient volume and made up to the mark with water. In an aliquot part of this solution the excess of iodine was determined by means of decinormal thiosulphate, and in another aliquot part of the solution the excess of the iodine was removed by means of a freshly prepared solution of sulphur dioxide of known strength and the total acidity of the resulting solution determined by means of decinormal sodium hydroxide, with phenolphthalein as the indicator. This method depends upon the reaction represented by the chemical equation $I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$, and hence for every equivalent of iodine used up theoretically 2 equivalents of acid should result, or, if 10 cc. of a decinormal solution of iodine be used up in this process, 20 cc. of decinormal sodium hydroxide should be required to neutralise the resulting solution exactly. If now a larger quantity than 20 cc. of decinormal sodium hydroxide be required, the excess is a measure of the sulphur trioxide resulting from the combustion of the sulphur, provided the solution of sulphur dioxide employed in the removal of the excess of iodine does not contain any sulphuric acid. By this method we were able to measure the quantity of sulphur trioxide formed in the burning of sulphur and to prove to our satisfaction that a certain amount of this substance did result in the combustion of sulphur. (That small quantities of sulphur trioxide are formed during the combustion of sulphur is evident from the fact that during the combustion, oily drops of sulphuric acid make their appearance on the walls of the tube.) This method has the disadvantage, however, that the solution of sulphur dioxide has to be prepared fresh every day, and the strength of the solution was found to be very subject to change and hence had to be determined practically for each determination. Fortunately, for the purpose of this investigation it was found that both of these gases could be determined (2) by means of a decinormal iodine solution, decinormal thiosulphate, and decinormal sodium hydroxide without resorting to the solution of sulphur dioxide. The method finally employed in our determinations is as follows:—

The gases resulting from the combustion of the sulphur are absorbed in a known volume of decinormal iodine solution. The liquid is then poured into a measuring flask of convenient volume and made up to the mark with water. In an aliquot part of this solution the excess of iodine is determined by means of a decinormal thiosulphate, and in this same portion the acid is determined by means of decinormal sodium hydroxide, phenolphthalein being the indicator. The quantity of iodine originally employed minus the quantity remaining unchanged as indicated by the thiosulphate gives the quantity of sulphur dioxide, and

Results of Experiments on the Combustion of 0·1 grm. of Sulphur in Air and Oxygen under the Conditions indicated in the Table.

No. of experiment.	Conditions.	Found. Sulphur burned to SO_2.	Found. Sulphur burned to SO_3.	Found. Total.	Per cent of sulphur burned to SO_2.	Per cent of sulphur burned to SO_3.	Total per cent of sulphur found.
1.	In air	0·09426	0·006884	0·101144	94·26	6·88	101·14
2.		0·09288	0·007614	0·100494	92·88	7·61	100·49
3.		0·09183	0·007690	0·09952	91·83	7·69	99·52
	Average, Series I.	0·09299	0·007396	0·100386	92·99	7·39	100·38
4.	In moist air	0·09153	0·00787	0·0994	91·53	7·87	99·40
5.		0·09578	0·00413	0·0999 (*a*)	95·78	4·13	99·91
6.		0·09153	0·00787	0·0994	91·53	7·87	99·40
	Average, Series II.	0·09294	0·00662	0·09956	92·94	6·62	99·57
7.	In air dried over sulphuric acid and lime	0·09049	0·009510	0·1000	90·49	9·51	100·00
8.		0·09373	0·006700	0·10043	93·73	6·70	100·43
9.		0·09316	0·006020	0·09918	93·16	6·02	99·18
10.		0·09456	0·005214	0·099774	94·56	5·21	99·77
	Average, Series III.	0·09298	0·006888	0·099868	92·98	6·88	99·87
11.	In dry air containing large quantity of carbon dioxide	0·09309	0·00657	0·09966	93·09	6·57	99·66
12.	In dry oxygen	0·09600	0·00314	0·09914	96·00	3·14	99·14
13.		0·09704	0·00240	0·09944	97·04	2·40	99·44
14.		0·09790	0·00270	0·1006	97·90	2·70	100·60
15.		0·09608	0·00347	0·09955	96·08	3·47	99·55
16.		0·09665	0·00257	0·09922	96·65	2·57	99·22
17.		0·09698	0·00230	0·09928	96·98	2·30	99·28
	Average, Series IV.	0·09677	0·00276	0·09953	96·77	2·76	99·53
18.	In moist oxygen	0·09893	0·00250	0·10143	98·93	2·50	101·43
19.		0·09776	0·00269	0·10045	97·76	2·69	100·45
20.		0·09720	0·00278	0·09998	97·20	2·78	99·98
	Average, Series V.	0·09796	0·00266	0·10062	97·96	2·66	100·62
21.	In a mixture of oxygen and carbon dioxide	0·09488			94·88		
22.		0·09763			97·63		
23.		0·09577			95·57		
24.		0·09689			96·89		
25.		0·09778			97·78		
26.		0·09743			97·43		
	Average, Series VI.	0·09673	0·00327 (*a*)	0·1000	96·73	3·27 (*a*)	100·00 (*a*)
27.	In equal parts by volume of oxygen and nitrogen	0·09552	0·0057	0·10122	95·52	5·70	101·22
28.		0·09233	0·0077	0·10003	92·33	7·70	100·03
	Average, Series VII.	0·09392	0·0067	0·10062	93·92	6·70	100·62
29.	In a mixture of 3 parts of oxygen and 1 part of nitrogen	0·09694	0·0029	0·09984	96·94	2·90	99·84
30.		0·09901	0·0023	0·10131	99·01	2·30	101·31
	Average, Series VIII.	0·09797	0·0026	0·10057	97·97	2·60	100·57

(*a*) By difference.

the excess of acidity over and above the amount which should result from the action of the iodine on the sulphur dioxide gives the sulphur trioxide resulting from the burning of the sulphur. Obviously, this method is based on well-known reactions employed in iodometry and acidimetry, and depends finally on the fact that the substances resulting from the action of iodine on sodium thiosulphate are neutral to phenolphthalein. The exact strength of the thiosulphate solution used was determined by means of Kahlbaum's re-sublimed iodine immediately before each experiment, and the exact strength of the iodine solution determined by means of the thiosulphate. The exact strength of the sodium hydroxide was frequently determined by titrating against weighed amounts of pure oxalic acid. The strict observance of these precautions is necessary if concordant results are to be obtained by this method. A specimen of crystallised sulphur was selected for the investigation. This was twice distilled and each of the first portions of the distillate were rejected. The product thus obtained was broken up into small pieces about the size of bird shot and preserved in a weighing bottle. In all our determinations 0·1 grm. of this was weighed out in a porcelain boat, which was then placed in a piece of Jena glass combustion tubing, 30 inches in length. One end of this long tube was drawn down to a tube of smaller calibre and connected with a train of five Drexel absorption bottles, the first four of which contained known amounts of tenth-normal iodine solution, and the last one from the tube contained a 2 per cent solution of potassium iodide. The last absorption bottle was connected with an aspirator bottle. The porcelain boat containing the sulphur was placed about four inches from the farther end of the tube away from the absorption bottles, and this end of the tube was then closed with a cork through which passed a piece of glass tubing about three-sixteenths inch in diameter, one end of which was drawn down so as to give an

opening about one-sixteenth of an inch in diameter into the larger tube. Through the smaller tube the air or oxygen required in the combustion of the sulphur was drawn by the aspirator bottle at the end of the train of absorption flasks. Care was taken so to regulate the combustion of the sulphur as to insure complete combustion and no volatilisation to the colder parts of the tube. The tube was of such length as to insure complete combustion of the sulphur long before any small amounts that might be volatilised could reach the absorption bottles. In a few of our experiments the sulphur to be burned was spread along the combustion tube over a considerable length, but always from the absorption bottles.

After the combustion was complete, the contents of the tube and bottles were transferred to a measuring flask and made up to the mark with the washings from the tube and absorption bottles. An aliquot portion was then titrated with sodium thiosulphate. From the number of cc. of iodine used up, the weight of the sulphur burned to sulphur dioxide was calculated. After adding a few drops of phenolphthalein, the acidity of the solution was determined by means of N/10 sodium hydroxide. The number of cc. of caustic soda required was recorded as "found acidity." From the quantity of iodine entering into reaction with the sulphur dioxide, the acidity resulting from the conversion of sulphur dioxide into sulphuric acid by means of iodine can be calculated. The found acidity minus the calculated acidity gives the acidity due to sulphur trioxide. From this the weight of the sulphur burned to sulphur trioxide may be calculated, and this, added to the weight of the sulphur burned to sulphur dioxide, gives the total weight of the sulphur burned. The results of our determinations are given in the accompanying table.

It will be seen from an examination of the results given in the table—

1. That there is a reasonable agreement between our determinations and those of Hempel, of the several amounts of sulphur dioxide and sulphur trioxide which result from the burning of sulphur in oxygen, especially when the fact that the combustion was carried out in a somewhat different manner in the two cases is kept in mind. According to Hempel, 2 per cent of the sulphur is burned to sulphur trioxide; according to our determinations, Series IV., 2·76 per cent of sulphur is burned to the trioxide.

2. It is further evident from our results that considerably larger amounts of sulphur trioxide are formed when sulphur is burned in air than when it is burned in oxygen. That such is the case may be seen from the results given in Series I., II., III., IV., and V. From an average of all of our results bearing on this point, it will be seen that about 2·5 times as much sulphur is burned to sulphur trioxide in air as is burned to sulphur trioxide in oxygen.

3. The results obtained in Series I., II., III., and in the single experiment No. 11 would seem to indicate that moisture, dryness, and the presence of increased amounts of carbon dioxide are practically without influence on the combustion of sulphur in air, and from Series IV. and V. it would seem that moisture is practically without influence on the combustion of sulphur in oxygen, and from Series VI. that carbon dioxide exerts but little influence on the combustion of sulphur in oxygen, the amount of sulphur trioxide being only slightly increased over the amount of this substance formed in dry and moist oxygen.

Finally, it would seem from the results of our experiments given in Series VII. that the increased production of sulphur trioxide in air as compared with oxygen is due in some way to the presence of nitrogen. It will be seen further from Series VIII. that a great diminution in the quantity of nitrogen as compared with the quantity present in the experiments of Series VII. and the quantity normally present in air causes a marked falling off in the production of sulphur trioxide.

It would seem therefore from our results that in the combustion of sulphur, nitrogen acts as a carrier of oxygen.

In support of this conclusion the fact may be mentioned that in the combustion of certain substances in air small amounts of nitrogen are also oxidised. For example, Kammerer (*Ber.*, x., 1684) proved the presence of nitrogen peroxide in the gases left after burning magnesium in air, by the characteristic odour and colour of the gas and by the formation of the iodide of starch on the addition of the potassium-iodide-starch reagent. Dixon and Russell have also observed that when an explosive mixture of carbon bisulphide and oxygen, containing small amounts of nitrogen, is ignited, some of the nitrogen is invariably oxidised (*Trans. Chem. Soc.*, 1899, pp. 75-610).

The formation of small amounts of one of the higher oxides of nitrogen during the burning of sulphur in air and the subsequent oxidation of sulphur dioxide thereby would afford the simplest explanation of the fact that considerably more sulphur trioxide is formed when sulphur is burned in air and in mixtures of oxygen and nitrogen than is produced when it is burned in pure oxygen or in mixtures of carbon dioxide and oxygen. — *American Chemical Journal*, xxxviii., No. 4.

THE

USE OF FELSPATHIC ROCKS AS FERTILISERS.*

By ALLERTON S. CUSHMAN,
Assistant Director, Office of Public Roads, and Collaborator, Bureau of Plant Industry.

(Concluded from p. 230).

The Effect of Fineness of Grinding.

From the evidence which has been submitted in the preceding pages it may be safely concluded that the potash contained in ground felspar is at least in some part available as plant food. The question whether it can be made sufficiently available under certain conditions to be an economical substitute for concentrated and soluble potash salts remains to be determined by systematic investigation. It may have been noticed in reading the account of the foregoing experiments that in only a few cases was the fineness of the felspar material described. Each investigator considered ground felspar fine material, whether it passed an 80-mesh or a 200-mesh sieve. A standard sieve containing 200 meshes to the linear inch has openings 0·0026 inch square. A sieve of 80 meshes to the linear inch has openings about 0·0007 inch square. It is never the case, however, that a material which has been ground so that it will just pass a certain sieve will consist of particles of uniform size corresponding to the size of mesh. All ground material contains a certain proportion of very fine particles, down to those which might be characterised as submicroscopic in size. The smaller the coarser particles of a given powder which has been ground in bulk the higher will be the proportion of very fine material. This is a very important point, because it is doubtless true that the amount of decomposition caused by the action of water on ground felspar is directly proportional to the active surface area presented by unit weights of the powder. To one who has not studied the matter, the rapidity with which surface area rises with fine grinding is very surprising. In a 200-mesh felspar powder, such as is supplied by the grinder for the pottery trade, the finest particles bear the same relation to the coarsest present as these latter would to fragments about 2 inches in diameter. As the surface area of a powder increases in inverse ratio to the diameter of the particles, it can be seen how quickly the availability due to active surface must increase with fineness in grain. No one would for an instant consider the possibility of fertilising land by scattering on it felspar

* From *Bulletin* No. 104, U.S. Department of Agriculture, Bureau of Plant Industry.

Table IV.—*Production (short tons) and Value (dollars) of Felspar, 1901—1905.*
("Mineral Resources of the United States," U.S. Geol. Survey, 1905).

Year.	Crude.		Ground.		Total.	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
1901	9,960	21,669	24,781	198,753	34,741	220,422
1902	21,870	55,501	23,417	194,923	45,287	250,424
1903	13,432	51,036	28,459	205,697	41,891	256,733
1904	19,413	66,714	25,775	199,612	45,188	266,326
1905	14,517	57,976	20,902	168,181	35,419	226,157

Table V.—*Price per Pound of Potash Unit in Felspar.*
(Cents per pound).

Potash contained in the felspar.	Cost of ground felspar per ton (2240 pounds).									
	$1.	$2.	$3.	$4.	$5.	$6.	$7.	$8.	$9.	$10.
3 per cent	0·015	0·030	0·044	0·059	0·074	0·089	0·104	0·119	0·134	0·149
4 ,,	0·011	0·022	0·033	0·044	0·055	0·067	0·078	0·089	0·100	0·111
5 ,,	0·009	0·018	0·027	0·035	0·044	0·053	0·062	0·071	0·080	0·090
6 ,,	0·007	0·015	0·022	0·030	0·037	0·045	0·052	0·059	0·067	0·074
7 ,,	0·006	0·012	0·019	0·025	0·032	0·038	0·045	0·051	0·057	0·063
8 ,,	0·005	0·011	0·017	0·022	0·028	0·032	0·039	0·045	0·050	0·056
9 ,,	0·005	0·009	0·014	0·019	0·024	0·029	0·035	0·039	0·044	0·049
10 ,,	0·004	0·009	0·013	0·018	0·022	0·027	0·031	0·035	0·040	0·045
11 ,,	0·004	0·008	0·011	0·015	0·020	0·023	0·028	0·030	0·034	0·040
12 ,,	0·004	0·007	0·011	0·015	0·018	0·022	0·026	0·029	0·033	0·037
13 ,,	0·003	0·007	0·010	0·014	0·017	0·021	0·024	0·027	0·031	0·034
14 ,,	0·003	0·006	0·010	0·013	0·016	0·019	0·022	0·026	0·029	0·032
15 ,,	0·003	0·006	0·009	0·012	0·015	0·018	0·021	0·024	0·027	0·030

fragments of an average diameter of 2 inches. Yet in grinding these fragments to an 80-mesh powder, we have not increased the active surface area as much as we should do by pushing on the grinding of an 80-mesh powder to the ultimate fineness attainable in mechanical processes. Grinding is making surface, and it can be shown that the availability of potash in ground felspar increases with the surface area. If felspar is ground so that it will pass an 80-mesh sieve, it will of course contain a certain proportion of very fine particles, some of which approach the limits of visibility under a powerful microscope. If we carry on the grinding of the material from 80-mesh to 200-mesh, the proportion of the very small particles is enormously increased. The smallest particles which we need to consider here are those which can be measured by a micrometer device connected with the microscope. These smallest particles have a diameter of about 0·0001 mm. Now, in order to make a specific example, we will consider the surface areas presented by 1 pound of felspar in different degrees of subdivision. First, in the form of a solid cube, then broken down to particles that could just pass an 80 and a 200 mesh sieve, respectively, and, finally, in the condition it would be if it were possible to grind all the material as fine as the finest particles which occur in an ordinary 200-mesh powder. The 1 pound of felspar in a solid cube would have a surface area of 29·3 square inches; particles capable of passing an 80-mesh sieve would give 8870 square inches; particles able to pass a 200-mesh sieve would give 24,905 square inches; and if it were possible to reduce the powder to particles 0·0001 mm. in diameter, there would result a surface area of 16,460,000 square inches.

If it were practically possible to collect 1 ton of felspar all in the state of the finest particles, as shown above, the surface area presented by the ton would be enormous—in fact, it would be equal to 256,000,000 square feet, 5877 acres, or more than 9 square miles. Now, although such grinding is out of the question at the present time, an ordinary 200-mesh felspar prepared for the pottery trade, which is valued at about 8 dols. per ton, contains a large proportion of very fine particles. The marvellous rise in the surface area attained by fine grinding is very well exhibited in the figures given, and it is undoubtedly true that previous experimenters have not paid sufficient attention to the percentage of very fine material in the ground felspar.

One opponent of the use of felspar has written ("The Potash in Crushed Rock," German Kali Works, New York):—

"What we call soil is rock of various sorts crushed or broken up by weather and other agencies. The crushed granite could hardly be more fertile than a good soil. When we think that an acre of soil 1 foot deep weighs over 3,500,000 pounds, we see what a drop in the bucket a few tons of ground rock really amounts to."

As a matter of fact, discussion of the value of a few tons of fine-ground potash-bearing rock, with its millions of square feet of surface area, can not be so easily brushed aside. It is true that the soil contains many fine particles; but those which, like felspar, suffer decomposition under the action of water have presumably been already decomposed, and this new material is to replace that which has been used up or removed. Each tiny particle of felspar provides only a small increment of potash, but in a ton of fine-ground material there are many billions of particles.

Cost of Ground Felspar.

Nearly all of the felspar which is at present ground to fine powders is prepared, as has been stated, for the pottery trade. For this purpose it is necessary to use mills with specially adapted linings so that the finished product shall not become contaminated from the contact with iron or steel. The production and cost of felspar, mainly for the use of the potteries, during five consecutive years, is shown in Table IV.

For fertiliser purposes the fine grinding of felspar could be done in iron mills similar to those which are used for grinding limestone in the cement industry. The only important points to consider would be the percentage of total potash present and the fineness of grinding. At the present time there are few data available on the cost of grinding felspar to a 200-mesh powder, but with modern machinery there is little doubt that it can be done much

more economically than would have been considered possible only a few years ago. Under the stimulus of the cement industry a great development has been made in recent years in the methods and art of fine grinding. Table V. is of interest, as it shows at a glance what the potash in ground felspar would cost if the percentage is compared with a cost of grinding varying from 1 dol. to 10 dols. per long ton.

The prices are given in cents per pound, so that if, for instance, rock carrying 8 per cent of potash could be delivered for 9 dols. per ton, the potash contained in it would be added to the land at a cost of 5 cents per pound. At 5 dols. per ton the cost per pound would fall to 28 mills. The figures are of course only applicable provided the potash in the ground material can be proved available as a plant food.

It must be remembered that the only real measure of available potash is that which is made use of by the crop. It is not likely that all the potash added, even in the form of soluble potash salts, is actually used, and the amount that can be supplied by ground rock is still an unknown quantity.

Possible Harmful Effects of Ground Felspar.

The question is frequently asked whether there is possible danger to the land in experimenting with the use of ground felspathic rock. It is well known that in some cases, notably with tobacco, injurious effects are produced by the continued use of the soluble potash salts, particularly the sulphate and muriate. Felspar grains of various sizes are normally present in many soils; it does not, therefore, seem possible that any harmful effect could follow the application of ground rock. As has been pointed out in an earlier portion of this paper, felspar consists of the alkaline elements, soda, potash, and lime, combined with alumina and silica. After decomposition, hydrated aluminium silicate, the essential base of all clays, is left behind, the alkalis and the silica being set free in a condition in which they can be absorbed by the root action of plants. It would seem, therefore, that whatever the value of the results obtained no possible harm can follow the experimental use of ground felspar in reasonable quantities.

Extraction of Potash from Ground Rock.

The discussion of the use of ground rock as a source of potash is not complete unless it includes the extraction of potash by chemical and electrical processes. If future experiments should demonstrate that fast-growing crops are dependent on very soluble forms of potash, the question of the extraction of this element from ground felspar becomes a matter of importance.

The extraction of potash from rock has not as yet been accomplished on a commercial basis, but it has been done in the laboratory, and the method has been published in a recent bulletin (*Bull.* 28, U.S. Dept. of Agriculture, Office of Public Roads). The full details of the investigation are too technical for insertion here, but if the processes described could be carried on at a cost low enough, the potash in ground rock could be rendered sufficiently soluble for all practical purposes. Briefly, the method consists in sliming the ground felspar with water to which a small quantity of hydrofluoric acid has been added. This slime is placed inside a suitable wooden vessel and a current of electricity is passed through it. The alkali set free by the action of the acid is carried away by the electric current, while the acid appears to be used over and over again. Finally, by combining the acid and alkaline products, a material is obtained in which the potash which has been set free is soluble and available. It is hoped that further investigation will result in some method based on these principles for making the vast quantities of potash contained in felspathic rocks completely available.

Conclusion.

A careful reading of the foregoing pages will show that no claim has been made that ground felspar is an efficient substitute, under all circumstances, for potash salts. The effort has been to present all the evidence which could be collected, both for and against the use of ground felspar as a fertiliser. The question is still open, and systematic and long-continued experimentation is the only possible method of obtaining conclusive information on the subject. The evidence so far obtained appears to indicate that under certain conditions and with certain crops felspar can be made useful if it is ground sufficiently fine. On the other hand, it is highly probable that under other conditions the addition of ground felspar to the land would be a useless waste of money. At the present stage of the investigation it would be extremely unwise for anyone to attempt to use ground rock, except on an experimental scale that would not entail great financial loss.

The subject must be approached conservatively, with due regard to business economy. Sensationalism and exaggeration invariably do harm. It is extremely unlikely that ground rock will ever entirely displace the use of potash salts, for its availability must inevitably depend upon many modifying conditions, such as the nature of the soil, the amount of moisture present, the character of the other fertilisers used, and the varying root action of different crops. With tobacco the results so far obtained have been encouraging, but it is possible that this plant, which is a voracious feeder, can make use of the potash in fine-ground felspar to a greater extent than other fast-growing crops, such as potatoes and the cereals, some of which mature in practically sixty days and must therefore find their plant food in a highly available condition.

THE USE OF SODIUM CARBONATE AND ZINC OXIDE IN SULPHUR AND ARSENIC DETERMINATIONS.

By W. C. EBAUGH and C. B. SPRAGUE.

A METHOD involving the use of sodium carbonate and zinc oxide for sulphur and arsenic determinations was devised by one of us (C. B. S.) some years ago, and has given uniform satisfaction in various assay offices for so long a time that an account of it should be made public.

One part of dry sodium carbonate and four parts of zinc oxide are mixed thoroughly. In the case of sulphur determinations a weighed sample of the material to be analysed, usually one-half grm., is mixed intimately with enough of the sodium carbonate-zinc oxide reagent to afford at least twice as much sodium carbonate as would be required by the sulphur, arsenic, &c., present, placed in a small porcelain dish, covered with the reagent, and heated to redness in a muffle for fifteen or twenty minutes. A shorter period of heating is usually sufficient, but the time here specified is ample for all cases. The residue is then extracted with water, boiled, filtered, the filtrate made acid with hydrochloric acid, precipitated with barium chloride, and the barium sulphate treated as usual.

In an arsenic determination the substance is treated as above until the alkaline solution is filtered from the residue. This filtrate is acidified with acetic acid, precipitated with silver nitrate, boiled for a few minutes, and then filtered. The precipitate of silver arsenate is washed thoroughly with hot water, and then dissolved in dilute nitric acid, its silver content being determined finally by titration with ammonium or potassium sulphocyanate in the usual way. Ferric sulphate is used as an indicator In calculating the arsenic present use the proportion :—

3Ag : 1As :: wt. of silver found : wt. of arsenic present.

The method has been tried successfully with various sulphides such as galenite, pyrite, arsenopyrite, chalcopyrite, sphalerite, &c.; with sulphates like gypsum and anglesite; and with metallurgical products like matte speiss, and flue dust. In the case of analyses of heavy spar the method is

not superior to the ordinary fusion with an alkali. The fact that the decomposition with sodium carbonate and zinc oxide has been employed for control and umpire assays upon ores in commercial work for so long a period without objection, is evidence that the results obtained by the method are accurate.

It will be seen that the method for sulphur is a modification of the well-known Eschka method, and that for arsenic is an improvement upon Pearce's method. The advantages of the decomposition described are :—(1) That the mass resulting from the heating is not fused, but can be removed readily from the dish and leached with water ; (2) the ease and speed with which sulphides, sulphates, arsenates, &c., are decomposed ; (3) no time-consuming subsequent evaporations are necessary ; and (4) the absence of a large quantity of alkaline and other salts from the solutions in which the precipitations of barium sulphate and silver arsenate are effected.—*Journal of the American Chemical Society*, xxix., No. 10.

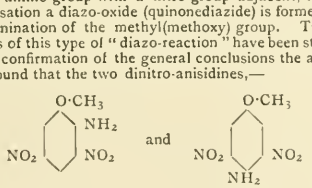
PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following completes the abstracts of Papers received during the vacation, and published or passed for publication in the *Transactions* :—

178. "*The Diazotisation of Dinitroanisidines and Related Compounds.*" By RAPHAEL MELDOLA and JAMES GORDON HAY. (*Trans.*, 1907, 1474.)

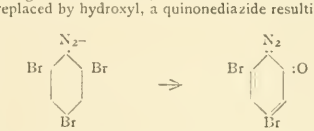
As the result of former researches, the conclusion has been reached that the configuration essential for the displacement of a nitro-group on diazotisation is that the mobile group must not only be in the ortho- or para-position with respect to the amino-group, but that there must also be another nitro-group or acid substituent in a position adjacent to the mobile group. When these conditions are not fulfilled and the methoxy-group is in the ortho- or para-position with respect to the amino-group with a nitro-group adjacent, then on diazotisation a diazo-oxide (quinonediazide) is formed with the elimination of the methyl(methoxy) group. Two instances of this type of "diazo-reaction" have been studied, and in confirmation of the general conclusions the authors have found that the two dinitro-anisidines,—



in which neither of the two sets of conditions above indicated is fulfilled, behave normally on diazotisation, losing neither nitro- nor methoxy-group. In the course of the present research, the authors have prepared 2 : 3-dinitro-4-aminophenol, the N-*acetyl* derivative of which crystallises in yellow needles melting at 199·5°. The free base is unstable, and could not be isolated. A comparative study of the products of diazotisation of this and the corresponding dinitro-*p*-anisidine has brought out very clearly the "loosening" influence of the methyl-group on the nitro-group, since under conditions in which the dinitro-anisidine loses a nitro-group on diazotisation the dinitro-aminophenol retains both nitro-groups. The 2 : 3 : 5-*trinitroaminophenol*, of which the acetyl derivative was described in a paper recently published by one of the authors (*Trans.*, 1906, lxxxix., 1935), has also been isolated, and the products of its diazotisation studied in a preliminary way.

179. "*Isomeric Change in Benzene Derivatives. Replacement of Halogen by Hydroxyl in Chlorobromodiazobenzenes.*" By KENNEDY JOSEPH PREVITÉ ORTON and WALTER WILLIAM REED. (*Trans.*, 1907, 1554).

In continuation of earlier work (Orton, *Proc. Roy. Soc.*, 1902, lxxi., 153 ; *Proc.*, 1902, xviii., 252 ; *Trans.*, 1903, lxxxvi., 796 ; 1905, lxxxvii., 99) on the transformations of halogendiazobenzenes, in which an atom of halogen is replaced by hydroxyl, a quinonediazide resulting, thus :—



a study has now been made of mixed symmetrical chlorobromodiazobenzenes. For this purpose, the diazo-compounds which are obtainable from 2 : 6-dichloro-4-bromo-, 2 : 4-dichloro-6-bromo, 4-chloro-2 : 6-dibromo-, and 6-chloro-2 : 4-dibromo-anilines have been used. 3-*Chloro*-5-*bromo*-*p*-*toluidine* (which has not been hitherto described) was also prepared for the same purpose.

From these experiments, which were carried out in the manner followed previously, two facts have been elucidated. The replacement of halogen by hydroxyl is not exclusively confined to the halogen atoms which are in the ortho-position with respect to the diazo-group. Some 20 per cent of the molecules of the diazo-compound lose an atom of halogen from the para-position, a *p*-quinonediazide being formed.

When all other conditions are alike (such as relative positions in the benzene ring, contiguity of other substituting groups, &c.), the displacement of the halogen appears to be independent of the nature of the halogen. Thus 80 per cent of the molecules of 2 : 6-dichloro-4-bromodiazobenzene and 4-chloro-2 : 6-dibromodiazobenzene respectively lose one atom of chlorine or bromine from the ortho-position ; again, 50 per cent of the molecules of 3-chloro-5-bromo-*p*-diazotoluene lose an atom of chlorine from one ortho-position (with respect to the diazo-group) and 50 per cent lose bromine from the other ortho-position.

The authors consider that the position to which the hydroxyl becomes attached will depend rather on the general symmetry and configuration than on the nature of the halogen atom occupying the given position.

180. "*A New Colouring Matter from* Nyctanthes Arbor-tristis." By ERNEST GEORGE HILL and ANNODA PRASAD SIRKAR. (*Trans.*, 1907, 1501).

The flowers of *Nyctanthes Arbor-tristis* yield a yellow dye soluble in water. On heating the aqueous extract in dilute hydrochloric acid, a reddish brown flocculent precipitate is formed. The greater part of this is soluble in alcohol, but cannot be crystallised from this solvent. If the alcoholic solution is gently warmed with a few drops of concentrated hydrochloric acid, a bright red sediment forms, and the solution loses most of its colour. This substance crystallises from pyridine or phenylhydrazine, and has the formula $C_{20}H_{27}O_4$. It is slightly acid, very sparingly soluble in most solvents, but readily in alkalis. It forms the *acetyl* compound $C_{20}H_{26}O_3{\cdot}C_2H_3O$, but contains no methoxyl groups. It gives neither phloroglucinol nor pyrocatechol on fusion with potassium hydroxide.

The flocculent precipitate gives a bromine compound, $C_{20}H_{15}O_{18}Br_5$, which yields bromoform on warming with potassium hydroxide.

The name *nyctanthin* is suggested for the red crystalline substance $C_{20}H_{27}O_4$.

181. "*The Velocity and Mechanism of the Reaction between Iodine and Hypophosphorous Acid.*" By BERTRAM DILLON STEELE. (*Trans.*, 1907, 1641).

The velocity and mechanism of the reaction between

iodine and hypophosphorous acid have been investigated under various conditions.

It has been found that the velocity of the reaction is independent of the concentration of the iodine provided this does not fall below a certain limiting value. This behaviour is best explained by the supposed occurrence of consecutive reactions of such a nature that the iodine takes no part in the slower or controlling reaction.

The reaction is unimolecular with respect to the hypophosphorous acid, and it is catalytically accelerated by hydrogen ions, the velocity under certain conditions being directly proportional to the concentration of the latter.

Since hydrogen ions are formed during the course of the reaction, the latter becomes autocatalytically accelerated in the absence of any large initial concentration of acid.

The further oxidation of phosphorous acid to phosphoric acid by iodine is one which is retarded by the presence of hydrogen ions. It should furnish therefore an example of autocatalytic retardation.

182. "*Succinic Acid and its Potassium Salts.*" By Hugh Marshall and Alexander Thomas Cameron. (*Trans.*, 1907, 1519).

In a previous paper (*Proc. Roy. Soc. Edin.*, 1905, xxv., 401), Cameron described the preparation of crystals of acid potassium succinate showing curved faces. The authors have now continued that research, giving further particulars of these curved crystals, and, more particularly, a description of the pure potassium salts themselves, since trustworthy data concerning these have not hitherto been published. The conditions of equilibrium for aqueous solutions containing potassium and hydrogen succinates were studied at various temperatures. At the ordinary temperature, solutions having the composition of the superacid salt, $KH_3(C_4H_4O_4)_2$, first deposit succinic acid; solutions having the composition of the acid salt, $KHC_4H_4O_4$, first deposit the superacid salt. Above 30—35°, however, the acid salt is in equilibrium with a solution having a similar composition, and it would also appear that at a consider ably higher temperature the same is true for the superacid salt.

It seems probable from the results obtained that the superacid salt is not merely a "molecular" compound, but that the complex ion $H_3C_4H_4O_4'$ exists in considerable proportion in the solution, especially at higher temperatures.

The acid salts, $KHC_4H_4O_4$, $KHC_4H_4O_4,2H_2O$, and $KH_3(C_4H_4O_4)_2$, were examined crystallographically; these, with the normal salt, $K_2C_4H_4O_4,2H_2O$, were the only potassium salts of succinic acid obtained within the limits of temperature covered by the investigation.

183. "*The Fluoresceins and Eosins from 4-Hydroxyphthalic, 4-Methoxyphthalic, and Hemipinic Acids.*" By Arthur Friedl, Charles Weizmann, and Max Wyler. (*Trans.*, 1907, 1584).

Resorcinol condenses readily with 4-hydroxyphthalic, 4-methoxyphthalic, and hemipinic acids, yielding the corresponding *hydroxy-*, *methoxy-*, and *dimethoxyfluoresceins*. Hydroxyfluorescein is very slightly fluorescent, whereas methoxyfluorescein, like ordinary fluorescein, is extremely so. Dimethoxyfluorescein is much less fluorescent than is methoxyfluorescein.

The corresponding tetrabromo-derivatives of these fluoresceins show corresponding differences in their fluorescent properties.

184. "*Researches on Anthraquinones and Phthaleins.*" By William Henry Bentley, Henry Dent Gardner, jun., and Charles Weizmann. (*Trans.*, 1907, 1626).

Hydroxymethylanthraquinones can be prepared in two stages from phthalic acid (or its derivatives) and the cresols (or their methyl ethers). A derivative of benzoylbenzoic acid is first prepared and subsequently condensed by sulphuric acid to the corresponding hydroxymethylanthraquinone:—

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_3Me\cdot OH \rightarrow$$
$$\rightarrow C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2Me\cdot OH.$$

The authors have employed two condensing agents for bringing about the first reaction, namely—(1) boric acid and (2) aluminium chloride, obtaining different results in each case where this was possible. Boric acid promotes condensation in the ortho-position, whereas aluminium chloride causes condensation to take place in the para-position with respect to the hydroxyl group.

A number of condensations of phthalic and hydroxyphthalic acids with the three cresols and *m*-4-xylenol have been effected.

185. "*Derivatives of Naphthacenequinone.*" (Part II.). By William Henry Bentley, Arthur Friedl, and Charles Weizmann. (*Trans.*, 1907, 1588).

The two nitrophthalic acids condense with *a*-naphthol yielding nitrohydroxynaphthoylbenzoic acids, $NO_2\cdot C_6H_3(CO_2H)\cdot CO\cdot C_{10}H_6\cdot OH$, which on reduction yield the corresponding amino-acids; the latter condense in sulphuric acid to aminohydroxynaphthacenequinones, which thus contains the amino-group in the benzene ring:—

$$NH_2\cdot C_6H_3\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_{10}H_5\cdot OH.$$

These derivatives dissolve in concentrated sulphuric acid with a much bluer, and in alcoholic potash with a much yellower, colour than is exhibited by 1-amino-6-hydroxynaphthacenequinone, which contains the amino-group in the naphthalene ring.

Hemipinic acid condenses with *a*-naphthol, yielding *hydroxydimethoxynaphthoylbenzoic acid*,—

$$(CH_3\cdot O)_2C_6H_2(CO_2H)\cdot CO\cdot C_{10}H_6\cdot OH,$$

which when heated with sulphuric acid appears to hydrolyse and also oxidise during the condensation, the product on analysis giving numbers corresponding with *trihydroxymonomethoxynaphthacenequinone*.

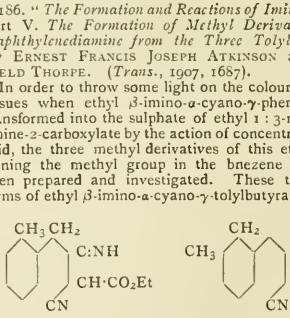
1:5-Dihydroxynaphthalene, being a di-*a*-naphthol, can condense with two molecules of phthalic acid, yielding *dicarboxybenzoyldihydroxynaphthalene*,—

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_{10}H_4(OH)_2\cdot CO\cdot C_6H_4\cdot CO_2H.$$

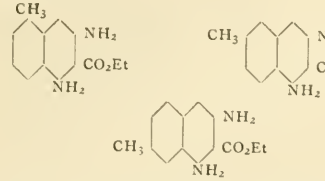
This acid, however, on condensation with sulphuric acid appears to lose one phthalic acid group, yielding a *trihydroxynaphthacenequinone*.

186. "*The Formation and Reactions of Imino-compounds.* Part V. *The Formation of Methyl Derivatives of* 1:3-*Naphthylenediamine from the Three Tolylacetonitriles.*" By Ernest Francis Joseph Atkinson and Jocelyn Field Thorpe. (*Trans.*, 1907, 1687).

In order to throw some light on the colour change which ensues when ethyl β-imino-α-cyano-γ-phenylbutyrate is transformed into the sulphate of ethyl 1:3-naphthylenediamine-2-carboxylate by the action of concentrated sulphuric acid, the three methyl derivatives of this ethyl salt, containing the methyl group in the benzene nucleus, have been prepared and investigated. These three isomeric forms of ethyl β-imino-α-cyano-γ-tolylbutyrate,—



pass on treatment with cold concentrated sulphuric acid into the corresponding methyl derivatives of ethyl 1:3-naphthylenediamine-2-carboxylate:—



These ethyl salts on hydrolysis yield the corresponding carboxylic acids, which readily evolve carbon dioxide, and pass into 1-methyl-5 : 7-naphthylenediamine, 2-methyl-5 : 7-naphthylenediamine, and 2-methyl-6 : 8-naphthylenediamine respectively.

Whereas the transformation of the meta-compound into the naphthalene ring at $-5°$ is, like the other cases investigated previously, practically quantitative, the yield of the naphthalene derivative from the ortho- and para-compounds is scarcely 10 per cent of the theoretical, the main product of each reaction being a phenolic base which is characterised by giving an intense colour with concentrated sulphuric acid.

The malachite-green solutions which were formed at the ordinary temperature, but not at $-5°$ in the reactions previously investigated, are therefore probably due to the formation of similar phenolic bases, since the naphthalene derivatives formed in the reactions do not themselves give colours with sulphuric acid. The following are the colour reactions of the three isomeric ethyl salts named towards concentrated sulphuric acid at the ordinary temperature.

Ethyl β-imino-α-cyano-γ-*o*-tolylbutyrate dissolves, forming an intense red-brown solution, which on dilution becomes first olive-green and finally yellow.

Ethyl β-imino-α-cyano-γ-*m*-tolylbutyrate forms a cherry-red solution, which becomes colourless on dilution.

Ethyl β-imino-α-cyano-γ-*p*-tolylbutyrate dissolves, forming an intense magenta-red solution, which on dilution becomes first violet, then blue, then green, and finally yellow.

No colour is formed in the case of the meta-derivative at $-5°$, but lowering of the temperature has no effect on the colour formation of the ortho- and para-compounds.

187. "*The Chemical Action of Radium Emanation.* Part II. *On Solutions containing Copper and Lead, and on Water.*" By Alexander Thomas Cameron and Sir William Ramsay, K.C.B. (*Trans.*, 1907, 1593).

Radium emanation, as is known, yields helium when allowed to stand alone or mixed with oxygen and hydrogen gases. When dissolved in water, the gaseous product is neon, containing a trace of helium, and in presence of copper nitrate, the product is argon, containing no recognisable trace of helium. The copper solution, after the emanation has decayed in contact with it, is found to contain a trace of lithium; at the same time, the weight of the residue, which consists mainly of sodium salts, is considerably increased. The experiments were carried out in glass bulbs.

The authors suggest as a hypothesis :—(1) That helium and the α-particle are not identical; (2) that helium results from the "degradation" of the large molecule of emanation by its bombardment with α-particles; (3) that this "degradation," when the emanation is alone or mixed with oxygen and hydrogen, results in the lowest member of the series to which the emanation undoubtedly belongs, namely, helium; (4) that if particles of greater mass than hydrogen or oxygen are associated with the emanation, namely, liquid water, then the "degradation" is less complete, and neon is produced; (5) that when molecules of still greater weight and complexity are present, as is the case when the emanation is dissolved in a solution of a copper salt, the product of "degradation" of the emanation is argon. They are also inclined to believe that the copper also is involved in this process of degradation, being reduced to the lowest member of its series, namely, lithium, and they suspect that, at the same time, sodium is produced in much greater quantity than lithium. Experiments on the gases evolved from thorium nitrate show that carbon dioxide is one of the products; this might be interpreted by the same hypothesis, in supposing carbon to be formed by the degradation of thorium, the highest member of the carbon series.

188. "*Indican.*" (Part I.). By Arthur George Perkin and William Popplewell Bloxam. (*Trans.*, 1907, 1715).

Indican, $C_{14}H_{17}O_6N,3H_2O$, crystallises from a mixture of benzene and alcohol in anhydrous prisms, m. p. 176—178°, and in this form can be readily re-crystallised from absolute alcohol. On hydrolysis with dilute acids in the presence of isatin, a quantitative yield of indirubin is obtained, as predicted by Beyerinck (*Proc. K. Akad. Wiltensch. Amsterdam*, 1899, ii., 120), but a theoretical yield of indigotin has not as yet been produced from it by a combination of hydrolysis and oxidation. When indican is digested with boiling dilute acid in absence of air, a complex reaction occurs, a trace of indole being formed together with dextrose (compare Hazewinkel, *Proc. K. Akad. Wetensch. Amsterdam*, 1900, ii., 512) and brown, amorphous substances. The main constituent of the latter, for which the name *indoxyl-brown* is suggested, has a similar composition, and closely resembles the chief constituent of indigo-brown (*Trans.*, 1907, xci., 295), with which it is, no doubt, closely allied, but, on the other hand, it is more soluble in alcohol, and differs from it in certain minor respects. It has been found possible to isolate as much as 30 grms. of crystalline indican from 1 kilogrm. of the leaves of the *Indigofera Sumatrana*.

189. "*The Occurrence of Quercitol* (*Quercite*) *in the Leaves of* Chamaerops humilis." By Hugo Müller.

This paper gives a short account of the occurrence of quercitol (quercite) in the leaves of *Chamaerops humilis*, the only species of the palm family indigenous in Europe.

These leaves in the dry state yield as much as 1·35 per cent of this substance, and, as it can be obtained from them by a very simple process, may form a suitable material for its preparation.

This quercite is the dextro-modification, and is identical with that obtained from acorns.

190. "*Cocositol* (*Cocosite*), *a Constituent of the Leaves of* Cocos nucifera *and* Cocos plumosa." By Hugo Müller.

Cocosite, isomeric with inosite, is contained in the leaves of *Cocos plumosa* and *Cocos nucifera*, and also in the so-called milk of the cocoanut. In general chemical character, it resembles inosite, and shows the characteristic rhodizonic acid reaction, but differs very widely in its physical properties, such as crystalline form, melting-point, and solubility in water.

A *hexa-acetate*, a *nitrate*, and *sulphonic acids* have been obtained and examined.

Cocosite still more closely resembles the quercenin found by Delachanel and Vincent in the acorn, and also the scyllit of Staedeler and Frerichs, recently re-investigated by J. Müller. It seems highly probable that these three substances are identical.

191. "*Inositol* (*Inosite*)." By Hugo Müller.

The difficulty of procuring a somewhat larger supply of material for the fuller investigation of cocosite suggested a previous study of the behaviour of the isomeric inosite, when submitted to the reactions contemplated for this purpose, as the results thus obtained would serve as a guide and indirectly effect an economy in the use of cocosite.

A considerable quantity of inosite, which had been prepared from cochineal, furnished the material for this investigation.

The behaviour of inosite hexa-acetate, when submitted to the action of a saturated solution of hydrogen bromide in glacial acetic acid in the manner described by W. H. Perkin, jun., and J. L. Simonsen, has been investigated, and also the reaction of hydrogen peroxide in conjunction with ferrous sulphate on inosite according to the methods devised by Fenton.

Monobromoinosite penta-acetate, two isomeric forms of *dibromoinosite tetra-acetate*, and also *inosite dibromohydrin* have been fully examined.

On treating the monobromo-penta-acetate with zinc-dust, it loses its bromine along with one molecule of acetic acid.

If, on the other hand, the dibromoinosite tetra-acetates are treated in the same manner, phenol and acetic acid are the only products.

The treatment of inosite by Fenton's method with hydrogen peroxide yields, with a transitory dark violet-blue coloration, besides some oxalic acid, a substance which has not yet been obtained in a definite form, but from which the barium rhodizonate and potassium-croconate have been prepared.

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, November 4th, 1907.

Mr. R. J. Friswell in the Chair.

"*The Determination of Indigotin in Indigo-yielding Plants.*" By Cyril Bergtheil and R. V. Briggs.

The accurate determination of indigotin in the indigo plant is of considerable importance, since a correct estimate of the efficiency of the process of indigo manufacture depends thereon. A method of precipitating indigotin from an extract of the plant in boiling water by means of ammonium persulphate, proposed by Rawson in 1904 and modified by the present authors, has been shown to give correct results by comparison with those obtained by fermentation of the extract by means of the indigo enzyme (*Journ. Soc. Chem. Ind.*, 1906, xxv., 729).

This method has been criticised by Orchardson, Wood, and Bloxam, and two alternative methods proposed, one of which, depending on the same principle, is said to give results identical with those obtained by the authors' method; whilst the other, depending on the precipitation of indirubin by the action of isatin in acid solution, indicates a considerably higher potential yield of indigotin in the plant extract used (*Journ. Soc. Chem. Ind.*, 1907, xxvi., 4). The authors' original method is now verified, and some minor modifications are recommended. It is shown that neither of the methods proposed by Orchardson, Wood, and Bloxam can be used in practice, since both lead to entirely erroneous results unless the exact indican content of the samples dealt with is previously known and the methods adjusted accordingly.

The conclusion that the isatin method may under certain circumstances indicate a higher indican content in a given extract than the persulphate method is not borne out by the authors' experiments.

"*Analysis of Indigo* (Part III.) *and of the Dried Leaves of* Indigofera arrecta *and* I. Sumatrana." By R. Gaunt, F. Thomas, and W. P. Bloxam.

A summary is first given of the results of the work on indigo carried out for the Government of India at the University of Leeds during the years 1905-1907. In the present paper the exact conditions were prescribed for the preparation of pure indigotin to serve as the standard on which the tetrasulphonate process for the estimation of indigotin is based. A reply was made to certain criticisms on the tetrasulphonate process; the defects complained of were shown to be due to want of proper precaution on the part of the operators. The methods in use for the estimation of indigotin in the leaf were described. The persulphate method was found altogether faulty, as the results obtained by it were too low. The new "isatin" method was found to give much higher results, and, moreover, the method is quantitative, as proved by its action on the glucoside indican which has recently been isolated in quantity by Messrs. A. G. Perkin and W. P. Bloxam. As a result of employing the isatin process the indigo leaf is demonstrated to be capable of yielding more indigotin than had previously been supposed. Again, the percentage of leaf present in the green plant has been under-estimated in India. It is insisted that these facts are in favour of the survival of the Indian indigo industry. To this must be added the discovery by the authors of a sample of dried leaf of *I. Sumatrana*, which was twice as rich in indigotin as any specimen of *I. Sumatrana* (the more highly valued Java or Natal plant). Finally, it was submitted that the work on the indigo ferment or enzyme had not been properly followed out, and that the present reports on the Indian manufacture are eminently unsatisfactory, for:—

(1) The colour giving value of the raw materials was seriously under-estimated, whilst (2) the indigotin value of the manufactured cake was over-estimated, and this owing to the persistent use of unsatisfactory methods of analysis in lieu of adopting the tetrasulphonate process.

FARADAY SOCIETY.

Ordinary Meeting, October 29th, 1907.

Mr. N. T. M. Wilsmore, M.Sc., in the Chair.

The Chairman announced that Sir Oliver Lodge had accepted the invitation of the Council to succeed the late Sir William Perkin as President of the Society.

A paper on "*The Electrolysis of Salt Solutions in Liquefied Sulphur Dioxide at Low Temperatures*" was communicated by Dr. Bertram D. Steele. (See p. 224).

A paper on "*The Action of Aluminium Powder on Silica and Boric Anhydride*," by Mr. F. E. Weston, B.Sc., and Mr. H. Russell Ellis, B.Sc., was read in abstract by Mr. Weston, who showed, on a small scale, some of the reductions described.

The authors have studied the action of aluminium powder upon boric anhydride and silica respectively. It is shown that in the case of boric anhydride the reducing action of the aluminium depends upon the fineness of both the aluminium and the boric anhydride, *e.g.*:—

(*a*) Mixtures in molecular proportions of the finest obtainable aluminium powder and powdered B_2O_3 which has passed through a sieve of 14,400 meshes to the square inch react at once, in the cold, when started with a fuse of Mg ribbon and BaO_2 powder.

(*b*) Mixtures in proportion of Al_2 to $2B_2O_3$ only react when heated to dull redness in a muffle furnace.

(*c*) Similar mixtures to (*a*) and (*b*), but using B_2O_3 that has only passed through a sieve of 3600 meshes to the square inch, only react when heated to 300° C. and dull redness respectively.

The products of the reaction were shown to be Al_2O_3 and mixtures of boron with aluminium borides, the latter predominating in the mixture containing molecular proportions and the former in the other mixture.

In the action of aluminium upon silica the authors used for the latter kieselguhr, precipitated silica, and fine silver sand. Here, again, the action took place more readily with the finer varieties of silica, the speed and energy of the reaction being in the order—precipitated silica, kieselguhr, silver sand.

The action took place in the cold with precipitated silica and kieselguhr on being started with a fuse of Mg and BaO_2, when the constituents in the mixture were in the ratio of $3SiO_2$ to 8Al; when the mixture contained the constituents in the ratio of $3SiO_2$ to 4Al the reaction only took place on heating the mixture to dull redness. When

sand was used the mixture had to be heated to a dull redness in each case before the action commenced, and in the mixture containing $3SiO_2$ to $4Al$ free sand and free Al were found in the product.

The products of the reaction contained in all cases Al_2O_3, silicon (as shown by the production of $SiCl_4$), and probably some silicides of Al.

Dr. R. Seligman suggested that some of the heat required in these reactions was furnished by the aluminium or boron, as the case may be, burning in the air. The fireproof slags obtained in many cases were being used for making acid-resisting crucibles and for other industrial purposes.

Dr. F. M. Perkin pointed out that the difficulty of getting a fusible slag in all cases prevented the preparation in a pure state of products like boron and silicon.

Dr. F. M. Perkin and Mr. L. Pratt read a paper on "*The Reduction of Metallic Oxides with Calcium Hydride*," and illustrated some of the reductions.

When copper oxide is mixed with calcium hydride in proportions corresponding to $2CuO + CaH_2 = 2Cu + CaO + H_2O$, and ignited by means of a match, a vigorous reaction ensues, and volumes of steam are given off. On cooling a black mass is obtained, which on treatment disintegrates, owing to solution of calcium oxide, and metallic copper in a state of fine division is obtained. Pyrolusite, hæmatite, and tin stone all behave in a similar manner. Zinc oxide appears not to be reduced. Lead sulphide and antimony sulphide both react vigorously, and during the reaction the mixture swells up considerably, rising up out of the crucible in a cylindrical form. Very little metal is produced, the bulk of the product being a dark grey mass, which appears to be a compound of the metal with calcium and sulphur.

Borax and boric anhydride also react with calcium hydride when the mixture is strongly heated in the muffle furnace. Silica in the form of fine sand only reacts after prolonged heating, but reaction takes place more readily when kieselguhr is employed. Wolframite and rutile only react with difficulty.

Experiments were also tried with metallic calcium and wolframite. In this case a particularly vigorous reaction takes place, the tungsten being melted and being obtained on cooling as a hard regulus. The heat is so great that the calcium oxide is also melted. Rutile is also reduced by calcium; the reaction, however, is not so intense, and the titanium and calcium oxide are not fused.

The action of metallic calcium upon metallic chlorides was also studied. Manganese chloride and cadmium chloride are readily reduced. When metallic calcium and strontium chloride are mixed together in molecular proportions and ignited by heating in an iron crucible by means of the blowpipe, reaction ensues: $SrCl_2 + Ca = CaCl_2 + Sr$. Very little metal, however, is obtained, probably owing to the formation of a subchloride, ClSr—CaCl. On adding two atoms of calcium the reaction is intensely vigorous, and the metal is obtained as a fused regulus. With barium chloride the reaction is less vigorous. With the alkali metals very vigorous reactions also take place.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, August 7th, 1907.

H. A. Lenehan, F.R.A.S., Vice-President, in the Chair.

The following papers were read:—

"*Note on Copper in Andesite from near Lautoka, Fiji.*" By H. I. Jensen, B.Sc. (By permission of the Council of the Linnean Society of New South Wales).

This paper describes the occurrence of lumps of copper ore weighing from 1 lb. in andesitic matrix. An analysis of a specimen showed that it contained 53¼ per cent Cu, 7¾ per cent Fe, and 21½ per cent S, the metallic portion being therefore a mixture of bornite and chalcocite. A microscopic examination confirmed the presence of these two minerals. The same minerals were found to occur in many of the normal andesites of the district in smaller quantity. A quantitative estimation revealed 0·034 per cent of CuO in the normal andesite. It appears from the examination of specimens obtained, that either copper ore has segregated out in the consolidation of the lava, or else, in the period of consolidation, magnetic vapours have extracted the copper from portions of the lava, and deposited it elsewhere in the mass. The copper distinctly belongs to the andesite magma of the district, and does not constitute a mere xenogenic included product. It is interesting to note that such a differentiation has there taken place in a true volcanic rock.

"*Analysis of a Specimen of Sea-water from Coogee, New South Wales.*" By C. J. White, Caird Scholar, University of Sydney.

The sample analysed was a surface water collected off Coogee, New South Wales, on October 9th, 1906. Specia attention was paid to the specific gravity determinations (for the calculation of which Buchanan's hydrometer No. 6 was used), for this gives the salinity directly, and indirectly gives very valuable indications of the various constituents present (the ratio of dissolved salts to one another being practically constant for all ocean waters). The results obtained, after combining the constituents in the generally accepted way, and omitting CO_2, were:—

NaCl	27·370	grms. per kilo.
$MgCl_2$	3·884	,,
$MgSO_4$	1·667	,,
$CaSO_4$	1·264	,,
K_2SO_4	0·887	,,
$MgBr_2$	0·072	,,
MgO (by difference)	0·048	,,
Total	35·192	

In the paper the results are also expressed in terms of 100 of halogen calculated as chlorine (*Challenger* method) and compared with the mean of 77 of Dittmar's analyses.

"*Note on the Action of Lime on the available Soil Constituents.*" By F. B. Guthrie, F.I.C., F.C.S., and L. Cohen.

The authors have investigated the changes that take place in the amounts of water-soluble and citric-soluble potash and phosphoric acid in limed soils in pots. Three kinds of soil were used, sand, garden loam, and clay. They find that in all cases the amount of mineral plant-food soluble in water had diminished to a considerable extent in the unlimed pots after standing for a month. The effect of liming has been to lessen this loss, but it does not appear to prevent it entirely. There is less water-soluble plant-food in the limed soils after a month than in the original soils, but more than in the untreated soils after a month. The action of lime has been either to prevent the loss of soluble plant-food that is going on or to increase it by rendering soluble fresh portions of the insoluble material of the soil. In the case of the citric-soluble ingredients, the effect of liming was much less marked. There is little or no loss of the citric-soluble plant-food in the case of the untreated soil after standing a month, and these figures are not appreciably affected by liming. In the case of the loam and clay soils, there is actually less citric-soluble phosphoric acid than in the untreated soils. In other cases the increase of citric-soluble plant-food is a very slight one. The action of lime is to largely increase the amount of nitrogen as nitrites, the nitrate-nitrogen is almost the same in the limed and the unlimed soils, except with the clay soil where the nitrates are diminished. The total nitrogen as nitrite and nitrate is increased by liming, and the action of lime would appear to be to favour the development of the nitrous organism in particular.

MISCELLANEOUS.

Royal Institution.—A Christmas course of illustrated lectures, adapted to a juvenile auditory, will be delivered at the Royal Institution by Sir David Gill, K.C.B., LL.D., D.Sc., F.R.S., on "Astronomy Old and New." The dates of the lectures are December 28 (Saturday), 31, 1907, January 2, 4, 7, and 9, 1908, at 3 o'clock.

Preparation of Aluminium Carbide. — Camille Matignon. — The large quantity of heat disengaged in the combination of aluminium with carbon, $C_3+Al_4=C_3Al_4$ +245 cals. (Berthelot) indicates that the union of the two elements would probably take place without the intervention of the electric furnace. The author proved the truth of this prediction as follows:—He made an intimate mixture of lamp-black with aluminium powder by working the two constituents up with terebenthene in the proportion of 24 parts of carbon to 70 or 140 of aluminium. Then he heated the mixture for 20 minutes in a Perrot furnace, and thus obtained a mass which had a yellowish or olive green colour. Under the microscope the crystalline carbide could be seen scattered in shining globules throughout the excess of aluminium. The latter was easily eliminated by washing either with cold hydrochloric acid or cold potash. When a specimen was decomposed with water a gaseous mixture, containing 96·36 per cent of methane and 3·36 per cent of hydrogen, was obtained. Iodine and sulphur when combining with one atom of aluminium set free a quantity of heat comparable with that disengaged with carbon. In order to make the first two elements unite with the divided metal it is only necessary to produce combination artificially at one place in the mixture, and this method is also successful with carbon, provided that an excess of aluminium is employed. The two elements also unite when they are heated in the oxyacetylene blowpipe flame. Finally, aluminium carbide can be prepared by allowing the chlorides of carbon to act upon the metal. The equation is $10Al+C_6Cl_6=2AlCl_3+2C_3Al_4$ +727·6 cals. The carbide is readily separated from the volatile aluminium chloride.—*Comptes Rendus*, cxlv., No. 17.

MEETINGS FOR THE WEEK.

WEDNESDAY, 20th.—Microscopical, 8. "François Watkins' Microscope" and "A Reply to Prof. Porter's and Mr. Everitt's Criticism upon my Paper 'On the Limits of Resolving Power for the Microscope and Telescope,'" by E. M. Nelson. "Mercury Globules as Test Objects for the Microscope," by J. W. Gordon. "Light-filters for Photomicrography," by E. Moffat.

— Society of Arts, 8. Inaugural Address of the 154th Session, by Sir Steuart Colvin Bayley, K.C.S.I., C.I.E., Vice-President and Chairman of the Council.

FRIDAY, 22nd.—Physical, 5. "Singing Sand from New England," by S. Skinner. Exhibition of a Micromanometer, by L. Bairstow. A Diabolo Experiment, by V. Boys. Exhibition of Gyroscope illustrating Brennan's Monorailway, by H. A. Wilson.

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By CLAYTON BEADLE and HENRY P. STEVENS.

Now that plantation rubbers are finding their way on to the market in increasing quantities, planters and all who are financially interested in rubber plantations are carefully following the trend of prices with a view of ascertaining what reception will be given to the much larger consignments that may be expected in the course of the next year or two, and whether the present prices relative to hard-cure will be maintained. They are also anxious to discover the best method of preparation and ultimate form in which to ship their product; that is to say, whether the manufacturer will prefer to buy in the form of "block," "sheet," "crepe," "biscuit" or any other form.

We are told, and there is no doubt about it, that the methods of coagulating and curing rubber are of the greatest importance in regard to the chemical and physical properties of the crude rubber, but this is not because a certain method of coagulating and curing has some mysterious and unexplained influence on the rubber, but because the rubber is obtained more or less free from the accompanying nitrogenous and other matters, mineral and organic. The best method of coagulating and curing is that which produces a rubber with the smallest proportion of substances which are not caoutchouc, provided that powerful chemicals and extremes of temperature have not been resorted to, as these might bring about an alteration in the chemical qualities of caoutchouc.

Hence prominence has recently been given to the observations of Henri, viz., that the reticulated structure of the coagulated rubber differs according to the coagulant employed. This has been quoted as proving that the method of coagulation affects the physical properties (nerve) of the raw rubber, which is quite possible. The mere fact of a difference of reticulation can, however, have no effect whatever on the properties of the ultimate *vulcanised* product, as it is obvious that at the temperature of vulcanisation the rubber is in a semi-liquid state, and all traces of structure disappear even if such microscopic structure has not been obliterated by the previous treatment of mastication between hot rollers.

It follows from this that the physical properties and nerve of raw rubber are not so intimately connected with those of the vulcanised product as many suppose, and Henri's observation supplies evidence in this direction.

With the advent of plantation rubber the brokers have naturally applied to it those rough but practical tests which have done duty for rubber in the past, and there has consequently arisen a great deal of discussion as to whether the best plantation products really possess in the same degree as hard-cure para those varied qualities summed up by the words "nerve" or "go."

Unlike plantation rubbers, which consist of little else besides the rubber hydrocarbon or caoutchouc itself, South American and African rubbers contain varying proportions of non-caoutchouc substances, so that there is a considerable loss in the processes of washing and drying to which they are submitted by the manufacturer in Europe. These losses have been estimated and have been found to vary from, say, 15 per cent in the case of hard-cure para to as much as 50 per cent in the lowest grades, the substances removed consisting of moisture, mineral impurities, nitrogenous bodies, resins, and possibly degenerative products of the rubber itself, due to the methods of curing, or rather want of them. Many of these impurities may be detected by inspection of the raw rubbers, and other impurities make themselves apparent in a want of resilience, or "nerve," and hence the latter served as a guide in valuing a crude rubber of this class. On the other hand, it is obvious that this method must fail if used to differentiate between high-class plantation rubbers containing but traces of resinous matter and other impurities. With low grade rubbers the want of "nerve" may be taken as indicative of the proportion of resinous and similar ingredients, but to differentiate high-class plantation rubbers by means of the "nerve" is to value the caoutchouc itself by physical qualities which are dependent on the homogeneity and compactness of the sample the temperature to which it has been exposed, and many other adventitious factors. Thus it is well known that a short exposure to a comparatively low temperature is very beneficial to the physical qualities of unvulcanised rubber, as will be apparent from the figures obtained in the tests to be described in this paper.

If any doubt is cast on the value of the so-called "nerve" as a criterion, we are told that experience has shown it to be the right method of valuation, and it is the view of "practical" men generally; but what applies to wild rubbers does not necessarily apply to well prepared plantation rubbers where experience on a manufacturing scale is wanting; indeed, outside the vulcanisation tests carried out in our laboratories we are unaware of any other published work upon which an opinion could be based.

Never before have brokers or manufacturers had presented to them a raw rubber of the purity of the best plantation rubbers, and it is obvious that both methods of valuation and manufacture must necessarily be modified. In our opinion the future criterion in the valuation of a plantation rubber will be based upon purity of the raw substance and the properties of the vulcanised product. It is obvious that as practically all rubber is vulcanised in the manufacture of rubber goods, it is the properties only of the vulcanised rubber which matter, and only those properties of the raw product which indicate useful properties in the vulcanised product should be taken into consideration in valuing the raw article.

As, however, many people regard the properties of raw rubber as all important for the purposes of valuation, we shall record the results of physical tests made in our laboratories on samples of hard-cure para and plantation rubbers. The samples were tested in the same manner as described in our previous paper on vulcanising tests with plantation rubbers. In each case the figure given is the mean of at least ten determinations. The samples examined were as follows:—

1. Sample of hard-cure para taken from a freshly cut loaf. The pieces were cut from sheets obtained by skinning off a few layers together. With a little practice such pieces can be peeled off by hand, thus yielding a sheet consisting of two or three layers firmly attached to one another.

2. Sample of hard-cure, portions of the same loaf, and obtained in the same manner as samples in No. 1, but dried in a desiccator until transparent.

3. Sample of best hard-cure para (unvulcanised) "cut sheet."

4. A quantity of hard-cure was masticated for just sufficient time to convert it into a homogeneous mass, which was then run into sheet form and the sheets tested after putting aside for a week.

5. Ceylon biscuit of the best quality procurable. The natural sheet form of the biscuit is adapted for testing without any further treatment. Of course the thickness of the sheet is not uniform, but in each case this was measured for each piece tested and the figure calculated to a sheet 1 mm. thick. The actual thickness of the biscuit tested did not exceed 1·5 mm.

6. Samples cut direct from a piece of block rubber. These samples were full of flaws and small holes as is generally the case with block, the pressure employed in compressing the sheets being insufficient to weld the whole to a compact mass free from flaws.

	Sample.	Tensile strength.		Per cent elongation		Per cent elongation after ruptured samples have been put aside for four hours.	Apparent specific gravity.
1.	Hard-cure	487		970		10·7	0·9271
2.	Hard-cure, dried	847		670		—	0·9209
3.	Hard-cure, "cut sheet"	2222		800		6·8	0·9376
4.	Hard-cure, masticated	430		300		—	0·9224
(*a*) 5.	Biscuit	468		500		2·0	0·9194
6.	Block	966		500		0	0·9060
	Block, another sample	927	929	950	672	0	0·9047
	" "	843		770		—	0·9151
	" "	981		470		—	0·9163
7.	Block	1436		810			
	Block, another sample	1472	1454	710	760	10·8	0·9231
8.	Block, masticated	518		300			
(*b*)	" "	483	500	550	425	—	0·9228
9.	Block, masticated and frozen	780		420		—	0·9214

(*a*) Mean of twenty tests.
(*b*) A small addition (1 per cent) of creosote was made during mastication of this sample.

7. Samples cut direct from a sample of very compact block almost free from flaws and air-bells.

8. A quantity of block masticated and treated exactly like the hard-cure in No. 4.

9. Sample of block pressed into sheets as in No. 8, but left in an ice chest for one week and tested two days after removal from ice chest.

(For a description of the methods of determining tensile strength and elongation, see our paper in the CHEMICAL NEWS, vol. xcvi., p. 57).

Owing to the air-bells and flaws in sample No. 6, the test pieces broke before they had time to get a really good stretching, and after rupture no elongation could be detected, although doubtless a slight elongation had taken place.

The figures under "per cent elongation at rupture" are only approximate, as it is very difficult to note the moment when the pieces begin to draw out and tear, which they do just before breaking.

The cut sheet as used in No. 3 is prepared by masticating washed and dried hard cure till perfectly homogeneous, and then compressing into a block. The block is next placed in an ice chamber and thoroughly frozen, and then cut into sheets with knives in a special machine.

A survey of the figures given in the accompanying table shows clearly the absolute futility of making tests on raw unvulcanised rubber samples unless the samples are treated in identically the same manner, both during and subsequent to the coagulation, washing, and drying. Take the case of the hard cure para. Strips pealed off a freshly cut loaf give a tensile strength of 487, but after drying 847, and after masticating till of uniform consistency, the tensile strength falls to 430. Yet, again, if the dried and masticated rubber be exposed for a long period to a low temperature, a tensile strength of 2222 is obtained. Which of these figures is to be taken as representative of hard-cure para?

Take the case of block rubber. Six samples of block from the same plantation, prepared in the same manner, but some compressed more strongly than others, give values from 843 to 1472. Take the same block and masticate it, the figure drops to 500. What figure this block would give if frozen and treated in the same manner as the hard-cure No. 3 it is impossible to say, but the figure would probably be higher, just as block No. 8 is higher than hard-cure No. 4, masticated and treated under the same conditions. The sample of block No. 9, which had been preserved in an ice chest for one week only, showed a tensile strength of 780 as against 500 before such treatment. The Ceylon biscuit No. 5 gives low values, but then it has not been subjected to the pressure that has been employed in producing the hard-cure and block samples; the figure is only 468 in the case of the biscuit as against 1454 in the well compressed block. If the tensile strengths of the raw rubbers as found on the market were independent of the mode of preparation, and could be taken as representative of the values of these rubbers to the manufacturer, then the sample of block should fetch about three times the price of the sample of biscuit, while as a matter of fact the prices of these two particular samples were about the same, and analysis showed the same percentage of caoutchouc within 1 per cent in both.

The figures for elongation are very difficult to interpret for the same reason as in the case of tensile strength, and much the same considerations apply. The elongation at rupture is naturally somewhat low with those samples giving a low tensile strength, and the fact that biscuit No. 5 and block No. 6 showed little or no permanent elongation is probably to be explained by the fact that they broke before they had stretched to their full capacity. In the case of the block No. 6 the reason is not far to seek, as the sample was a mass of fine air-bells. The biscuit No. 5 did not show this structure on mere inspection, but on cutting a thin section and examining it under a microscope it was at once apparent that the biscuit contained a number of minute air-bells.

Perhaps the most striking proof of the influence of the conditions under which crude rubber is prepared on its physical properties may be gathered from the figures for the "apparent" specific gravity. The specific gravity of biscuit No. 5 is low, corresponding with low tensile strength. That of block No. 6 is lower still, but this is due to the greater number of large air-bells, the more compact block No. 7 giving a higher specific gravity. The hard-cure No. 2 is denser than the block. After compressing into a sheet the density of course is much increased (compare No. 8 with No. 6, from which it was prepared), but the necessity of heating the block has reduced its tensile strength; on the other hand, on freezing for one week the tensile strength has improved without materially affecting the specific gravity. The hard-cure "cut sheet" No. 3 has the highest specific gravity of any of the samples examined, which is no doubt due to the enormous pressure to which the masticated material is subjected in the course of manufacture as already explained.

Chemical Society.—Research Fund.—A meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before Monday, December 9th, 1907. Those Fellows who received grants in December, 1906, or whose grants allotted in December of previous years have not been closed, are reminded that reports must be in the hands of the Hon. Secretaries not later than Monday, December 2nd, next.

RESEARCHES ON THE SEPARATION OF THE EARTHS OF THE YTTRIUM GROUP.

By A. BETTENDORFF.

NOTE.—The renowned investigator of the chemistry of the rare earths, Dr. Anton Bettendorff, who died here on October 28th, 1902, left behind him a very carefully planned experimental study of the separation of the earths of the yttrium group. I have already communicated some of the results of this study to various authors (*cf.* Bohm, "Die Darstellung der Seltenen Erden," Leipzig, 1905, i., p. 480; "Abegg's Handbuch der Anorgan. Chemie," Leipzig, 1906, iii., Part I., p. 317). The complete description of the experiments in question will be all the more interesting to those chemists who are engaged in the investigation of the rare earths. Dr. Bettendorff left the work nearly ready for publication; for the purpose of reproduction here it has only had to be slightly altered and some additions made from the notes he left.—E. RIMBACH, Bonn-a-R.

Two different materials, orthite and gadolinite, were used for the following experiments on the separation of the earths of the yttrium group; these were both treated by partly different methods of separation. The results I obtained are therefore described separately in the following pages according to the materials employed.

I. ORTHITE.

The decomposition of large quantities of orthite by degrees provided me with a considerable amount of earths of the yttrium group. They had been freed from earths of the cerium group by repeated treatment with potassium sulphate, and were distinguished by a decided yellow colour, so that it seemed probable that they contained a large amount of terbium earth. Their nitrate solution gave a strong absorption spectrum of Bahr and Bunsen's erbium earth, and indications only of the bands of didymium and samarium. Their equivalent weights varied between $\overset{II}{RO}$ = 89·40 and 94·10 from orthites of different origin.

Separation by Crystallisation of the Formates.

When the earths were treated with cold dilute formic acid, care being taken to avoid heating, they dissolved to a faintly rose-red liquid, which was quite clear. After several hours the separation of a salt began, and, when accelerated by stirring with a glass rod, it was completed in twenty-four hours. The salt which separated was removed from the mother-liquor, and the latter was evaporated over lime under diminished pressure at the temperature of the room. The crystals which formed were removed separately, until the mother-liquor had a syrupy consistency and the rose-red colour had quite disappeared. The five fractions thus obtained had the following properties.

No. I. Small, almost colourless crystals. On ignition carbon separated, and they gave a dark yellow earth, the equivalent weight of which had risen to $\overset{II}{RO}$ = 103·0. The solution of the nitrate showed a decided diminution of the amount of earths giving absorption spectra. The spark spectrum of the chloride still showed the yttrium lines very faintly.

No. II. Small rose-red crystals. Yellow oxide. Nitrate solution giving strong absorption spectrum of Bahr and Bunsen's erbium earth. Spark spectrum showing yttrium lines. Equivalent weight of the oxide $\overset{II}{RO}$ = 99·0.

No. III. Small, very faintly rose-red coloured crystals, the oxide of which is light yellow. Spark spectrum of the chloride giving yttrium lines. Absorption spectrum fainter than in Fraction II. Equivalent weight $\overset{II}{RO}$ = 95·34.

No. IV. Larger, almost colourless crystals, containing a very light grey oxide. Spark spectrum of the chloride shows clearly the yttrium lines. Nitrate solution giving only a faint absorption spectrum, $\overset{II}{RO}$ = 93·17.

No. V. Mother-liquor, colourless, syrupy, shows only a faint absorption spectrum of Bahr and Bunsen's erbium earth. The spark spectrum of the chloride gives very bright yttrium lines. Oxide almost white, equivalent weight $\overset{II}{RO}$ = 81·36.

This series of experiments shows that in the first difficulty soluble fractions of the formates of the earths of the yttrium group, an earth of higher equivalent weight can be concentrated, as M. Delafontaine stated (*Ann. Chim. Phys.*, [5], xiv., 238; *Jahresber.*, 1878, p. 255); he thought it was terbium earth. The experiments also show that the second, third, and fourth separations contain Bahr and Bunsen's erbium earth, and that the yttrium earth remains mostly in the mother-liquor.

By many systematic repetitions of the method described above with the separate fractions, finally the earths of the yttrium group of orthite were decomposed into three fractions, which possessed the equivalent weights $\overset{II}{RO}$ = 120·0, $\overset{II}{RO}$ = 91·70, $\overset{II}{RO}$ = 80·50.

The Earth $\overset{II}{RO}$ = 120·0.

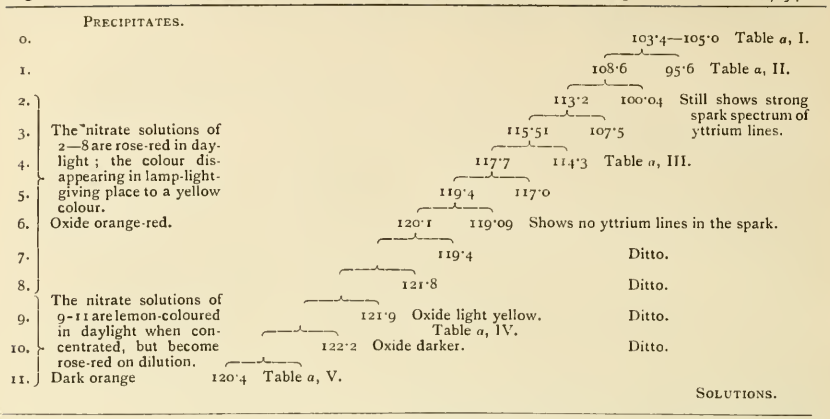
The colour of the earth $\overset{II}{RO}$ = 120·0 was deep orange-yellow. A concentrated solution of its nitrate in a layer 0·1 m. thick gave the absorption spectrum shown in Table I., which proves that the traces of earths of the cerium group which remain in ytterite earths, even when carefully purified with potassium sulphate, especially didymium and samarium earths, are concentrated in the most difficultly soluble formates by treating with formic acid. The table further shows that the fraction $\overset{II}{RO}$ = 120·0 was quite free from Bahr and Bunsen's erbium earth.

After the nitrate of the earth $\overset{II}{RO}$ = 120·0 had been treated with potassium sulphate, to remove didymium and samarium, according to the method I have described, allowing to stand (*Liebig's Ann.*, cclvi., 160), it was shown by the subsequent partial precipitation with dilute ammonia solution that a mixture of gadolinium and terbium earths was present. It was possible to obtain, firstly, a brown oxide of equivalent weight $\overset{II}{RO}$ = 121·57, and, secondly, a very light yellow oxide of equivalent weight 119·90 (gadolinium).

The Earth $\overset{II}{RO}$ = 91·70.

The second fraction $\overset{II}{RO}$ = 91·70, obtained on treating with formic acid, contained chiefly the earths giving absorption spectra and also a considerable quantity of yttrium earth, which could be detected by the spark spectrum. The oxide was still decidedly yellow, and thus probably contained terbium. As no further appreciable decomposition was effected on again treating with formic acid, the systematic partial decomposition of the nitrate was attempted in order to split it up further, and this was carried out in such a way that the greater part of the yttrium earth still contained in the oxide was removed.

The first separations, which were obtained by following the directions of Bahr and Bunsen (*Liebig's Ann.*, cxxxvii., 1), had an equivalent weight of $\overset{II}{RO}$ = 98·40 to 94·22, the ninth gave $\overset{II}{RO}$ = 91·22, and the twentieth $\overset{II}{RO}$ = 82·0. This fraction gave a colourless solution, and the spectroscopic examination of the syrupy solution in a layer 0·1 m. thick revealed indications only of absorption bands. $\lambda = \mu\mu$ 6400, 5356, 4853, 4506 were measured. The chloride of this fraction showed a very intense yttrium spark spectrum. By putting together the nineteen fractions and further partially decomposing the nitrate, a considerable amount of oxides was again separated as the final fractions; they consisted chiefly of yttrium earths. After repeating the process four times the earths of weaker



basicity when put together had an equivalent weight of RO = 103·40 to 105·0. Their colour was light orange-yellow. As a syrupy solution of the nitrate in a layer 0·1 m. thick they showed the absorption Spectrum I. shown in Table *a*. The chloride gave a strong yttrium spark spectrum.

Separation by means of Sodium Sulphate.

It had been found that a concentrated solution of the nitrates of these oxides 103·4 to 105·0, when treated with a supersaturated solution of sodium sulphate gave precipitates of double sulphates, which dissoived in water with difficulty and contained oxides of a darker yellow colour, The nitrates obtained from these showed in the spectral apparatus a decided decrease of the earths giving absorption spectra, and their chlorides gave only a faint spark spectrum of yttrium. In the mother-liquor, on the contrary, nearly white oxides are contained; they show a very strong absorption spectrum and yttrium earth spark spectrum.

The oxides of the precipitate further differ from those of the mother-liquor very considerably in equivalent weight. Moreover, it appeared that after repeating the precipitation with sodium sulphate, the double sulphates which are insoluble in it can very soon be obtained free from yttrium earth; their equivalent weight then rises rapidly, and the colour of the oxide becomes dark orange-yellow.

The most convenient method of treating with sodium sulphate was found to be as follows:—The concentrated solution of the nitrate was as nearly as possible neutralised, and then mixed with ten to fifteen times its volume of a sodium sulphate solution saturated at 30—35° in a flask closed with a cork, and the mixture was allowed to stand for twelve hours. Then a dense precipitate of the sodium double salt separated, and above it, if the experiment was satisfactory, there was a still supersaturated solution of sodium sulphate, which contains the parts of the double sulphate easily soluble in it, namely, the yttrium and the erbium earths.

Ten grms. of the oxides are dissolved in as little as possible dilute nitric acid. The solution seldom amounts to more than 20 cc. 150 grms. of crystallised sodium sulphate are dissolved in 150 cc. of water in a stoppered flask, first putting the salt into warm water, and then mixing the two liquids when it is completely dissolved. Care is taken not to reach a temperature of 33°, because then difficultly soluble anhydrous sodium sulphate is separated. It is then tested for supersaturation by throwing in a small crystal of Glauber salt; then the Glauber salt which separates is again dissolved, so that the precipitated insoluble double salt can be separated by filtration. The earths are recovered from the filtrate in the usual way.

The difficultly soluble double sulphates thus obtained are heated with a dilute solution of oxalic acid for some time; they are thus completely converted into oxalate, and after washing, igniting, and extracting the sodium carbonate with water, they yield pure earths, the nitrate solution of which is further precipitated with a supersaturated solution of Glauber salt. The accompanying summary shows the course of the treatment of the earths of equivalent weight RO = 103·40 to 105·0, mentioned above.

Table *a* shows in Nos. II. to V. the observed changes in the absorption spectra, which were all determined in syrupy solutions, with layers 0·1 m. thick.

The experiments I have just described give the following results:—After the earths of the yttrium group have been brought to an equivalent weight RO = 91·70 (see above) by repeated treatment with formic acid, a large part of the yttrium earth being thus removed, by a series of partial decompositions of the nitrates, another considerable proportion of the yttrium earth was removed (see above) so that the equivalent weight rose to RO = 103·4 to 105·0. On treating with sodium sulphate, from the sixth precipitation onwards, yttrium-free double salts can be separated, the oxides of which have the same colour and almost exactly the same equivalent weight as the first fraction RO = 120·0 (see above) obtained by systematic repeated treatment with formic acid.

It may be said that just as yellow oxides first separate as formates, so also on treatment with sodium sulphate the first double salts which separate contain yellow oxides. In other words, both the formates and sodium sulphate double salts of the yellow oxides are difficultly soluble.

I consider that the yellow oxides obtained by the two different processes are practically identical. This opinion is confirmed by the fact that the yellow earths obtained with sodium sulphate give darker to orange-red oxides in the precipitates, while those of the solutions (see above) contain light yellow oxides.

A further confirmation of my supposition is to be found in the fact that it was possible by means of a long series of partial precipitations with dilute ammonia to decompose the yellow ytterite earths of orthite of equivalent weight RO = 120—119, obtained by treatment with sodium sulphate, into fractions of RO = 123·80—123·30, which had a brown colour, like the gold precipitated with iron vitriol, then a yellow fraction of RO = 121·30—120·80, and finally a nearly white fraction of RO = 119·7 (gadolinium).

The above-mentioned brown terbium earth precipitated with ammonia and ignited, with RO = 123·80, is a dark brown or almost black glassy material. On dissolving in nitric acid a considerable quantity of gas is evolved (O ?) while the terbium earth obtained by igniting the oxalate is lighter in colour and gives no gas when treated with nitric acid.

When gently heated in hydrogen the terbium earths turn quite white. On very strongly heating they darken more or less. When heated in a current of air the earths, which have become grey again, acquire their original orange-yellow or brown colour.

The quantity of earths of orthite giving absorption spectra, which were mentioned above, was only small. As from the method of separation they still contained yttrium earth, a closer examination of them was for the present deferred.

The Earth RO = 80·50.

It only remains to add with regard to the earth obtained as the last fraction (see above) in the separation with formic acid, that it must consist chiefly of yttrium earth. Perhaps it contains ytterbium. It is almost white, and the equivalent weight as well as the spark spectrum indicate that it contains yttrium earth. The syrupy solution of the nitrate in a layer 0·1 m. thick shows indications only of absorption bands of Bahr and Bunsen's erbium earth.

In its purification by a series of systematic precipitations in acid nitric acid solution of the oxide by H. Rowland's method, a shining white yttrium earth was separated; it possessed an equivalent weight RO = 75·17. As syrupy nitrate it showed no trace of absorption lines. On account of its properties and more especially because of the agreement of its RO with Cleve and Rowland, I consider it to be pure (see below).

II. Gadolinite.

I had at my disposal 1 kgrm. of selected gadolinite which I had obtained from the chemical manufactory of Dr. L. C. Marquard, of Bonn. When finely powdered it was readily decomposed by sulphuric acid, and by the usual methods 434 grms. of raw earths were separated from it.

To separate the cerium group from the yttrium group the solutions of the nitrates of these earths were treated with potassium sulphate.

Two litres of a saturated potassium sulphate solution were added to 200 grms. of the earths dissolved in nitric acid, and 300 grms. of finely powdered potassium sulphate were added to the liquid in a stoppered flask. The whole was then left for several days, being repeatedly strongly shaken, until the solution above the precipitate of cerite earths-potassium double sulphates had become clear, and a thick layer of it no longer showed any didymium absorption lines. This occurred after five or six days. It was then filtered, and washed with about 1 litre of saturated potassium sulphate solution.

A layer 2 decimetres thick of the faintly red solution of the ytterite earths-potassium sulphate showed the following bands:—

Scale divisions of the apparatus.	Wave-lengths.	
14·78	6500	Er α
15·06	6388	X α
18·37	5404	These bands were observed by Krüss and Nilson in the holmium material from wöhlerite and thorite from Brevig, and were not named
18·61	5352	X γ
19·23	5222	Er β
19·39	5190	
21·25	4865	X δ
23·50	4555	X ζ

All these bands appeared comparatively very faintly.

Separation of the Double Sulphates by Crystallisation.

The faintly rose-red solution of the double sulphate was left in a large porcelain dish to evaporate at the temperature of the room, and the salt which separated removed from time to time. The first crystallisations, consisting of a mixture of rose coloured double sulphate, potassium nitrate, and potassium sulphate, gave, after dissolving in water containing nitric acid, precipitating with oxalic acid, igniting, and extracting the potassium carbonate by washing, a slightly yellow oxide with equivalent weight RO = 86·36.

The second crystallisation, which resembled it in appearance and had the same constitution, gave an oxide RO = 85·75.

The third and fourth crystallisations gave oxides of RO = 85·52 and 85·64.

The residual, very faintly coloured mother-liquor contained an oxide RO = 86·59.

These experiments show that no appreciable separation of the earths had taken place when their double sulphates were subjected to fractional crystallisation.

Separation by Auer von Welsbach's Oxide Method. (*Jahresber. d. Chem.*, 1883, 357).

When the mother-liquor, RO = 86·59, was treated by Auer v. Welsbach's oxide method, the first separation gave an oxide of RO = 93·45, the second RO = 95·65, and the third 91·12. The mother-liquor had an equivalent weight RO = 80·60. Thus by this method a decided decomposition and separation of the earths was effected, and all the above mentioned earths of the ytterite group were therefore treated in this way.

In the first series of decompositions an oxide RO = 80·60 remained behind as mother-liquor, in the second series an oxide RO = 81·80, and in the third RO = 83·24. These residues of the three series contained chiefly yttrium earth. The oxides were faintly yellow in colour, their nitrate solution was colourless, but the absorption spectrum showed that very small quantities of erbium earths were present in them. The traces of didymium oxide, which were still contained in the ytterite earths of gadolinite, in spite of careful treatment with potassium sulphate, had accumulated in the above residues. The Table β shows in II. and III. the absorption spectra of the residues of the first and third series, compared with a spectrum of didymium nitrate in I.

The equivalent weight of the fractions first separating, *i.e.*, the weaker bases, increased with the number of the series. In the eight series consecutive fractions with the following equivalent weights were obtained:—(1) RO = 104·00, (2) RO = 128·3, (3) RO = 130·54, (4) RO = 127·0, (5) RO = 126·3, (6) RO = 124·0, (7) RO = 123·8, (8) RO = 120·0, (9) RO = 115·20, (10) RO = 101·60. (Residue containing yttrium earth).

Fractions 1 to 3 must, from their preparation and equivalent weight, contain scandium and ytterbium earth. As a matter of fact, according to L. F. Nilson's statement (*Jahresber. d. Chem.*, 1880, 302), 1·2 grms. of scandium earth could be separated from the fractions by means of potassium sulphate.

The decomposition of the yttrite earths of gadolinite was proceeded with by Auer v. Welsbach's method, and it was always carried out in such a way that the greatest part of the yttrium earth, *i.e.*, the oxide of strongest basicity and smallest equivalent weight, was first removed. Then the fractions of the oxides of weaker basicity of the different series were collected by themselves. The earths giving absorption spectra then formed the middle fractions of all the ytterite earths of gadolinite.

After continuous laborious work controlled by repeated determinations of the equivalents of the fractions the following were obtained:—

1. Ytterbium material.
2. Erbium earth material (Er, Ho, Tm, Dy).
3. Yttrium earth material.

Ytterbium Earth.

There were 22 grms. of these earths obtained as the first fractions of ten series of decompositions:—

(1) RO = 126·37 (excluded), (2) 130·80, (3) 130·75, (4) 131·70, (5) 131·26, (6) 131·10, (7) 130·90, (8) 131·80, (9) 131·35, (10) 131·60 (11) 130·8.

When they were put together the concentrated solution of the nitrate, which had a distinctly reddish tinge, showed a faint absorption spectrum, which is marked No. IV. in Table δ. (Twenty grms. of oxide in 100 cc.; thickness of the layer, 0·057 m.). The thulium lines appear strengthened, which agrees with the statements of Soret, Marignac, and Cleve. The oxides were free from yttrium, or at any rate no yttrium lines could be seen in the spark spectrum of the chloride.

The fractionation of the ytterbium material was effected with dilute ammonia solution in the usual way. It was now, for the first time, observed that the first and last fractions mostly had a smaller equivalent weight than the middle fractions. The first might contain scandium. In the last fractions the lowering was to be ascribed to the presence of an earth giving an absorption spectrum in which thulium bands were visible.

By removing these fractions, finally an ytterbium earth could be obtained, which, when partially precipitated with dilute ammonia, gave a series of fractions with constant equivalent weight RO = 131·0.

The ytterbium earth of equivalent weight RO = 131·0 forms a perfectly snow-white powder, and shows indications only of absorption bands in concentrated solution of the nitrate. On partial precipitation with dilute ammonia it gives gelatinous precipitates, which, when digested on the water-bath, quickly become denser, and finally crystalline. Under the microscope it is possible to detect thin hexagonal leaflets, which are completely isotropic. They are probably a basic nitrate of the earth. From the material separating in the preceding purification, which, as we saw, gave fractions of lower RO than RO = 131·0, by a fresh separation ytterbium earth of RO = 131·0 could be obtained.

In the course of the separations also an ytterbium earth of rather higher RO, *i.e.*, RO = 131·5, was obtained; it also was snow-white and had the same properties as the foregoing preparations. This was really to be expected from the composition of the original material (see above), for it contains fractions with RO = 131·80.

Which of the three ytterbium earth preparations is the purest can, in the present state of our knowledge, be decided only by spectroscopic methods. Nilson (*Comptes Rendus*, xci., 56 and 118; *Jahresber. d. Chem.*, 1880, 299) found for his ytterbium earth preparation obtained from euxenite $R^{III} = 173·0$. This corresponds to $RO^{II} = 131·29$.

Erbium Earths.

In the approximate separation of the ytterbium earths from the erbium and yttrium earths by Auer von Welsbach's method, a series of fractions was obtained, the equivalent weights of which were RO = 129·0—120·0 They gave strong absorption spectra of the erbium earths, and showed faint yttrium lines in the spark spectrum of the chlorides. To them were added the residues giving absorption spectra of the preparation of the ytterbium earths. The oxides were collected separately, and fractions were obtained with RO = 129·0—127·0, 126·5, 123·0, 120·0.

First, the fractions RO = 129·0—127·0 were decomposed into several series by systematic partial precipitation with dilute ammonia, and it was then found that a considerable quantity of ytterbium earth was still present in them. After as complete a separation as possible had been effected, the earth had an equivalent weight of RO = 126·5.

Hitherto it has always been believed that the earth which is most decidedly rose-red in colour is the one which contains the most erbium earth (Cleve, *Comptes Rendus*, xci., 381; O. Dammer, "Handb. d. Anorg. Chem.," iii., 43). I observed now that the fractions with this property are those which also possess a fairly high equivalent weight RO = 127·0—129·0, and from which, by systematic treatment, oxides of the equivalent weight of the ytterbium earth RO = 130·0—131·0 can be separated. The more the latter are removed from the fractions the more yellowish brown coloured become the earths of lower equivalent weight RO = 126·5—122·0 which remain behind. It looks to me as if the ytterbium earth obtains its beautiful rose-pink colour, which it shows when prepared from the ignited oxalate, from an oxide of lower equivalent weight and stronger basicity. In other words, it seems to me that no rose-red erbium earth exists, that the oxide which has hitherto been taken for it, and which has the equivalent weight $RO^{III} = 126·63$, $R^{III} = 166·0$, is only an impure ytterbium earth. We may compare with this phenomenon the blue coloration given to alumina by traces of cobalt or the green coloration given to zinc oxide by the same impurity.

In the fractions RO = 127·0—129·0 the thulium is present greatly concentrated, as may be seen from the spectral Table γ, I., and II., and it seems to me not improbable that the oxide which colours the ytterbium earth rose-red is thulium oxide.

Oxides of RO = 126·5.—The oxides of equivalent weight 126·5, which were dirty yellowish red coloured, were put together, and as they amounted to only a few grms., it was not possible to decompose them further by partial precipitation with dilute ammonia. However, I tried whether the solution of the formate gave uniform separations on fractional crystallisation by slow evaporation.

The earth RO = 126·5 dissolves in cold dilute formic acid if all heating is avoided, giving a clear rose-red solution. When evaporated over lime at the temperature of the room it gives beautiful small crystals of a decided rose-red colour which possess an oxide of RO = 126·5. The mother-liquor contains an oxide of the same equivalent weight. Thus no separation has been effected.

Oxides of RO = 120·7—123·8, 119·0—124·0. — These earths were dirty yellow coloured, and are clearly a mixture of different oxides. It almost looks as if an oxide of constant RO = 124·7 could be obtained from them. But it was impossible to continue the research in this direction also, because the quantities of the oxides were so small. A characteristic property of these earths is the fact that they are dissolved by nitric acid, giving a lemon-yellow solution, and the solution can be evaporated to a yellow syrup. If they are dissolved in a larger quantity of water, the lemon colour changes to rose-red, and on evaporation a rose coloured syrup is now obtained. If a lemon coloured nitrate solution is evaporated with sulphuric acid, lemon coloured crystals are obtained. The nitrate solution, which has become rose-red, gives, under the same conditions, rose-red salts. As regards this change of colour it is evidently the same phenomenon as is observed with the earths of orthite (see above). If the absorption spectra of the nitrate solutions of these oxides of RO = 119—124·0 are examined, both when they are yellow and red, they show no appreciable difference. However, the spectra are essentially different from those of the original material. Thus it is found that the holmium lines appear much strengthened. This is seen very clearly if we compare No. IV of Table δ with No. III. of Table γ. The oxide which belongs to the first spectral table has an equivalent weight of RO = 126·5, and the other has an equivalent weight of RO = 120·0—123·8 (119—124). The strength of the bands ascribed to erbium is the same in both tables, but the holmium bands are much stronger, and also new bands of holmium appear, which are otherwise visible only in very concentrated solutions of the original material. The well known fact that holmium earth possesses a stronger basicity than erbium earth is thus confirmed, for the earths 120·0—123·8 were obtained on partial fractionation with dilute ammonia, after the separation of the erbium earth.

If the comparison of the absorption spectra is extended

to Table *a*, Nos. IV. and V., it is found that here only holmium bands appear. This absorption spectrum is that of a nitrate solution of the dark orange-red terbium earths of equivalent weight 120·4 (see above) obtained from orthite; these earths were separated by means of a supersaturated solution of sodium sulphate, and were found to contain holmium, but to be free from erbium.

Hence we must conclude that the separation of holmium earth from erbium earth proceeds decidedly more quickly and more completely in supersaturated sodium sulphate solution than by partial precipitation with dilute ammonia.

As the terbium earth RO = 120·4, rich in holmium earth, gives a yellow solution, and thus behaves in this respect like the earths RO = 120·0—123·8, it must be supposed that holmium and its salts give yellow solutions.

Yttrium Earth from Gadolinite.

From 1 kgrm. of selected gadolinite, after the removal of the earths of the cerium group with potassium sulphate (see above) and of the weakest bases of the yttrium group by Auer von Welsbach's oxide method (see above), I obtained a liquor very rich in yttrium earth containing about 194 grms. of earth. It still contained traces of didymium and erbium earth, and the raw earth gave an equivalent weight of RO = 81·40. The liquor, the volume of which was 600 cc., was fractionally precipitated with potassium ferrocyanide in portions of 200 cc., according to Rowland's method (*Johns Hopkins Univ. Circular*, May, 1894; CHEMICAL NEWS, lxx., p. 68; also *Am. Chem. Journ.*, xvii., 154). To each 200 cc. 30 cc. of concentrated nitric acid and 500 cc. of water were added, and 50 cc. of a solution of potassium ferrocyanide, saturated at the temperature of the room, and diluted with 50 cc. of water, were added to the whole; the mixture was stirred, and allowed to stand for twelve hours. Soon a turbidity appeared, and gradually became more marked, until after the twelve hours a fine heavy reddish white precipitate had settled. As it could not be separated by filtration (it runs through the thickest filter-paper) the clear supernatant liquid was carefully drawn off. The precipitate, consisting of ferrocyanides, was decomposed by boiling with aqueous ammonia, the hydrated oxides thus obtained were filtered off, carefully washed, and ignited. Then the residue was dissolved in hydrochloric acid, and separated from the iron of the potassium ferrocyanide by means of oxalic acid. To purify further the oxide obtained from the oxalate it was dissolved in nitric acid and again precipitated with oxalic acid. When ignited and washed with water to remove all traces of alkali, the first oxide thus obtained by partial precipitation with potassium ferrocyanide was an earth of a decided yellow colour; its equivalent weight was RO = 87·0. It was found that the traces of the erbium earths of the original material were concentrated in it. A second precipitation with 10 cc. of potassium ferrocyanide solution, diluted with the same volume of water, gave a further precipitate, which, when treated in the same way, gave an earth of RO = 84·7. By systematically proceeding in this way oxides with continually decreasing equivalent weights were obtained; they became lighter as the RO diminished, and finally became white, when their ferrocyanides could readily be filtered. Finally, there remained in the solution an earth which could not be precipitated with potassium ferrocyanide, and which was separated with oxalic acid. After purification it had an equivalent weight of 76·0—76·58. This part was removed separately, while the oxides with the higher RO were again put together in order to separate again by fractionation the parts of equivalent weight RO 76·0—76·58.

When about 25 grms. of this yttrium earth of RO = 76·0—76·58 had been prepared, and it was found that no trace of the absorption bands of erbium earth was to be observed in the syrupy solution of the nitrate, while, on the other hand, bands of didymium appeared very clearly, it was treated with potassium sulphate to remove the latter constituent. The syrupy nitrate solution, which had been neutralised as far as possible by prolonged heating on the water-bath, was diluted with much water, poured into a flask which contained saturated potassium sulphate solution and a considerable quantity of finely-powdered solid potassium sulphate. The total volume of the liquid amounted to 700 cc. After the action had been allowed to continue for two days, the mixture being occasionally strongly shaken, a small quantity of a reddish precipitate of the double sulphate of didymium was obtained. When the action and shaking were continued for a longer time, after about eight days a copious precipitate of glittering white double salt resulted. After a further action, lasting three weeks, the precipitate was separated by filtration; the filtrate of about 650 cc. I denote by the letter A. The precipitate was washed five or six times with saturated potassium sulphate solution, and the washings collected by themselves. These I shall call C and the washed precipitate *c*. The equivalent weight determinations of the purified oxides of these fractions gave for A an RO = 75·69, for C an RO = 75·7, and for *c* an RO = 76·82.

The quantity of the oxides of A and *c* amounted to 11·5 grms. They were perfectly white in colour, as syrupy nitrate gave no trace of an absorption spectrum, and their chlorides gave a brilliant yttrium spark spectrum. The quantity of oxide of C was 13 grms. It was yellowish in colour, showed clearly the absorption bands of didymium, and contained considerable quantities of yttrium, as the spark spectrum of the chloride indicated.

In another series of systematic precipitations with potassium ferrocyanide 39 grms. of yttrium earth with RO = 76·2 were obtained. It was treated as before, and the nitrate was freed from didymium by means of potassium sulphate. Exactly the same phenomena were observed, and at last an yttrium earth with RO = 75·55 and free from didymium was obtained. The part containing didymium possessed an RO = 76·9, and also contained large quantities of yttrium earth.

The following conclusion may be drawn from these experiments. By the aid of Rowland's method it is possible to get fairly quickly an yttrium earth of equivalent weight RO = 76·0. In it all traces of didymium oxide have accumulated. If an attempt is made to remove this by means of potassium sulphate, the formation and separation of didymium potassium sulphate is quickly effected. But in addition a slow formation and separation of yttrium potassium sulphate takes place, and it does not appear to be so easily soluble in potassium sulphate as has hitherto been believed. In the solution, according to the volume, a larger or smaller quantity of yttrium potassium sulphate always remains, and it contains an yttrium of lower RO than the precipitate. The higher RO of the latter cannot be explained by the presence of traces of didymium, and it is more probable that the rise in the value is due to another earth.

If, finally, an attempt is made to purify further the yttrium earth of equivalent weight RO = 75·55 by H. Rowland's method a yellowish ferrocyanide is obtained, which is easy to filter and to wash, but the earths separated from it show only small differences in equivalent weight, differences which lie almost within the limits of error in determining them by converting the oxides into anhydrous sulphate.

I sent to Prof. H. Kayser, who is occupied with the determination of the spectrum of yttrium earth, the sulphates of a small quantity of yttrium earth from gadolinite RO = 75·3 as well as from orthite with an RO = 75·17 (see above). He informed me that the preparations agree with one another in the chief lines, but that the yttrium earth from gadolinite shows another series of lines which is missing in the yttrium earth of orthite, but which can be seen clearly in a samarium earth prepared by me (*cf. Liebig's Annalen*, cclxiii., 164). As the yttrium earth in question gives no absorption spectrum, I must conclude from this statement of Prof. Kayser's that the samarium preparation mentioned above is not pure, but contains

another earth, which is also present in my yttrium earth from gadolinite. The yttrium earth RO = 75·3 from gadolinite would therefore also contain another earth.

In the continued systematic fractionation by Rowland's method with potassium ferrocyanide described above I had removed the greater part of the yttrium earth from the whole quantity of about 194 grms. of earths of RO = 81·40, and obtained :—

31·4 grms.	RO = 75·33	They were perfectly white.
27·0 „	= 75·80	
7·7 „	= 76·10	
52·6 „	= 76·2—76·8	They had a very faint tinge of yellow.
34·0 „	= 77·12	Somewhat more decided tinge of yellow than the preceding fractions.

In addition there were a few grms. of fractions with RO = 79·15—96·0; their colour became more decidedly yellow as the RO increased.

Moreover, by this treatment I obtained 40 grms. of a decidedly orange-yellow coloured oxide with an RO = 108·4, as the other end of the fractions first separated by potassium ferrocyanide. In this orange-yellow oxide the traces of earths giving absorption spectra which the original liquid still contained (see above) were much concentrated, with the exception of the didymium oxide which collected in the fractions with smaller RO. A syrupy nitrate solution of the orange-yellow oxides RO = 103·4 showed in a layer 6 mm. thick the absorption spectrum represented in Table E 1, which shows only erbium and holmium lines. The bands of didymium do not appear at all.

But these oxides were not always free from traces of yttrium earth, as may be deduced from the spark spectrum of the chlorine compound. Their orange-yellow colour points to the presence of a considerable amount of terbium earth, and in order to remove this I employed the method used to separate the terbium earth in the working up of orthite (see above), namely, separation in slightly supersaturated sodium sulphate solution. When the concentrated cold solution of the nitrate of the earth was added to the cold (at about 15°) supersaturated sodium sulphate solution, only a slight precipitate of a white salt resulted. It was filtered off after two days. The quantity of deep orange-red oxide obtained from it amounted to only 5·2 grms with RO = 116·75, the amount of earths used being 40 grms.

But the oxide which was separated from the filtrate had also a decidedly orange-yellow colour, in contrast to the earlier experiments. When 10 grms. of it were mixed with a sodium sulphate solution at 40° a copious white precipitate separated. The formation of terbium sodium sulphate thus seems to occur, not with $Na_2SO_4.10Aq.$, but either with $Na_2SO_4.7Aq.$ or the anhydrous salt, Na_2SO_4. This is confirmed by the phenomenon that the above-mentioned filtrate gave a precipitate on heating on the water-bath. Its oxide was orange-yellow, while the earth oxide of the part not precipitated, *i.e.*, that remaining in the solution, was white.

Moreover, the treatment with sodium sulphate did not produce an essential decomposition of this mixture of earths. The absorption spectra 2 and 3 of Table E show this. No. 2 is perfectly similar to No. 1 as regards the number and relative intensity of the bands, with the difference that in 2 some have become unmistakably fainter, while the bands at 538 appear broader than in the former spectrum. In No. 3 all the bands are visible, though weakened. The relative intensities of the bands have somewhat altered when compared with 1 and 2; thus the band 645·7—642 has become somewhat more strongly marked than the neighbouring band on the left, and 536·8—538 shows the same phenomenon. No other decided changes can be detected. The spectra were always determined in a layer of syrupy solution 6 mm. thick.—*Liebig's Annalen*, ccclii., 88).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, October 18th, 1907.

Sir W. Ramsay, K.C.B., F.R.S., President, in the Chair.

This meeting was held in the Theatre of the Royal Institution, by kind permission of the Managers.

The President, in opening the proceedings, said :—Professor Fischer needs no introduction to you; but I may remind you that he was asked to give the Faraday Lecture in 1895. At that time his health precluded him from coming to England, and we have now to congratulate him that his health has greatly recovered, and ourselves especially on his having come among us to-night to deliver the Faraday Lecture. I shall not, however, take up any more time, but at once ask Professor Fischer to deliver his address.

Professor Fischer, speaking in German, then delivered the Faraday Lecture on "Synthetical Chemistry in its Relation to Biology" (see Chemical News, xcvi., pp. 207 *et seq*).

In presenting the Faraday Medal to Prof. Fischer at the conclusion of the lecture, the President said :—Before I call on Sir Henry Roscoe, I have great pleasure, Prof. Fischer, in the name of the Chemical Society in handing over to you this medal as a testimony of our great regard for you as our foreign member and of our affection for you as a man.

Sir Henry Roscoe—Mr. President, Ladies and Gentlemen, I have had the good fortune to hear many Faraday Lectures. I remember with pleasure the eloquence of Dumas; the charm of Wurtz, and the thought and beautiful diction of Helmholtz; but, Mr. President, I do not think that any of our Faraday Lectures has awakened greater interest than the one to which we have just listened; and this, not only because Prof. Emil Fischer is a master of his subject, and because he has laid before us work mainly accomplished by his own inventive brain and his own able hands, but also because the subject of the application of synthetical chemistry to biology which the lecturer has so ably brought before us is one which at the present moment is exceeded in interest and importance by no other branch of the science, not even—if I may be allowed, in the presence of the President, to say so—by that of radio-activity. Of the nature and character of the work which Prof. Emil Fischer has accomplished, the Fellows of the Chemical Society are good judges. When some years ago we learned that Emil Fischer had synthesised the sugars, all chemists were loud in their expressions of satisfaction and admiration. How much greater will those expressions be now when we learn what success has attended the apparently almost insoluble problem of the synthesis of the proteins.

If the one resembles the ascent of some unconquered Swiss peak, the other may be compared with the far greater feat of the attempt to reach the top of Mount Everest. But even supposing the last thousand feet of the mountain have proved to be too much for the strength of the mountaineer, yet the most important result has been achieved, for the route has been laid down and the directions given by which subsequent explorers may gain the summit. As Emil Fischer has already succeeded in this synthesis of the sugars, so he has pointed out the method by which he himself, as we all hope, or others following in his footsteps, will succeed in fully unravelling the constitution of those chemical mysteries, the proteins. By this grand work he has won for himself the admiration of us all—of all those who are interested in scientific discovery; and for bringing this subject before us in so able a manner I have the honour and pleasure of proposing a vote of thanks.

Sir James Dewar—Mr. President, Ladies and Gentlemen, I am exceedingly grateful to the Council for the honour which they have done me and more especially the Institution by asking me to second the admirable and eloquent vote of thanks which Sir Henry Roscoe has proposed. I assume that this has been conferred upon me as a tribute to the great man whom we have come here, Sir, to honour. For some thirty-four years, Faraday held the Chair which I have had the honour of holding, I am sorry to say, for now nearly thirty years. I cannot help thinking that the last portion of your address, in particular where you deal with the aims and method of the investigator, as well as the part that has been put so prominently before us by Sir Henry Roscoe, would have specially appealed to Faraday. Sometimes we have too great brilliancy in investigation. We have been told that the foundations of our science are being shaken, that we are living in an age in which the chemistry of the past will disappear, and that we shall have to reconstruct it on an entirely new basis. Now, Sir, I think you have conferred, by your work, the greatest honour upon the chemistry of the past. You have worked along the beaten lines of scientific investigation founded by Liebig, followed by Hofmann, Wurtz, Kekulé, and Baeyer, and have shown that, by following these ancient tracks, you can now assimilate new ground in a manner which these chemists would never have believed possible. In that way, Sir, you have consolidated the science of chemistry. However much, as Sir Henry Roscoe pointed out, we may wonder and admire radium, still we cannot but admit that the chemistry of carbon is the most extraordinary of that of all the elementary bodies, and that you, Sir, have done more than any man living to convince us of the possibility of yet further achievements in organic synthesis. What you have done would, I think, have appealed very much to Faraday, from the fact that you have worked in this magnificent, steady, undespairing, but yet successful way. There is a very admirable story of your great countryman, Luther, which represents the spirit of Faraday. Some very inquisitive person was anxious to obtain from Luther his opinion as to whether certain passages in the Scriptures were canonical or apocryphal, and Luther replied that the saints who particularly appealed to him were those of whom no marvellous stories had been recorded; who lived their lives without pretence like other people, and who did not desire to make themselves notorious. I am perfectly certain that was the mind of Faraday, and that is the mind of Emil Fischer. The man is sometimes greater than his work, and we admire you, Sir, not only for your work, but as a man. May I say that in coming here you have done a double honour to the Royal Institution. Perhaps you may be unaware of it. It has sometimes been said that the greatest discovery that Davy ever made was Faraday. You can hardly dissociate the one from the other. Now you have selected spontaneously this date for the first lecture of the season, although the Royal Institution really does not open until Christmas, and to-morrow is the centenary of the discovery of the alkali metals by Sir Humphry Davy. I do not know whether you knew this fact—but you have come here, and you have adorned both the names of Faraday and Davy by lecturing in the same room, which is practically in the same condition and at the same table where they have so often discoursed. I have to convey to you the hearty thanks of all the members of the Institution. We wish you long life to continue your great labours to adorn science, not only Germanic science, but the science of the world.

The Chairman having put the vote to the meeting, it was carried with acclamation.

Professor Fischer, speaking in English, said—Mr. President, Ladies and Gentlemen, I owe you my sincere thanks for the kind recognition which you have been so good as to extend to my modest endeavours. I have felt exceedingly honoured in having received this invitation of the Chemical Society to come here to deliver the Faraday Lecture, and to pay homage to the great discoverer who so often on this very spot announced the results of his wonderful researches. But it affords me a keener pleasure to recall on this occasion the constant friendly intercourse which has existed during many generations between the English and the German men of science, and which has led to much happy exchange of scientific thought.

PHYSICAL SOCIETY.

Ordinary Meeting, November 8th, 1907.

Dr. C. Chree, F.R.S., Vice-President, in the Chair.

Mr. J. M. Gordon was elected a Fellow of the Society.

Dr. Fleming, in opening the Discussion on Mr. Campbell's paper "*On the Use of Variable Mutual Inductances*," asked the author how his method compared in accuracy with the Carey Foster method, using a commutator to add up the impulses. He had frequently measured mutual inductance by determining the self-inductances of the primary and secondary joined in series, with the windings first helping each other and then opposing each other. He asked if the author's methods were applicable when dealing with the high frequencies used in wireless telegraphy.

Mr. A. Russell agreed with the author in thinking that mutual inductance was sometimes easier to calculate and easier to measure than self-inductance. The variable mutual inductance standard shown was very compact, and would be a great acquisition to a physical laboratory. In calculating self-inductance the variable current density over the cross-section of the wire sometimes brought in serious difficulties. The measurement of self-inductance in these cases might possibly be made by Mr. Campbell's method, but the limitations introduced into his formulæ by the assumption that the back E.M.F. was proportional to the rate at which the total current was changing would have to be considered.

Mr. Campbell, in reply to Dr. Fleming, said the methods of measuring mutual inductance described in the paper were more convenient and direct reading than that of Carey Foster, although they were not so absolute. They were of higher accuracy than the difference-method, in which the primary and secondary were put in series and their combined self-inductance measured both with the windings helping and opposing. In reply to Dr. Fleming and Mr. Russell, the methods of measurement described were not intended, in general, for use with high frequencies of the order of those used in wave telegraphy, where resonance methods appear to be the only ones available. Mr. Campbell mentioned that the correction for the small inductance of the rheostat in method (B) could be got rid of by making the rheostat of constant inductance, this being attained by running a manganin and a copper wire side by side with a travelling contact across them, the current entering by the copper at one end and leaving by the manganin at the other.

A paper "*On a Freehand Graphic way of Determining Stream Surfaces and Equipotentials*" was read by Mr. L. F. Richardson.

The paper shows that where an accuracy of 1 to 3 per cent of the range is sufficient, solutions of the equation—

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0$$

may be obtained by drawing equipotentials and sections of stream surfaces, and amending them freehand until the chequers which they form take the appropriate shape at each point of the field. The method can only be applied in certain types of symmetry, as where V is constant along each line of one or other of the following families of lines:—(i.) parallel straight lines, (ii.) circles with their centres on a common axis and their planes normal to this axis, (iii.) radii from a point, (iv.) the normals common to

the two surfaces of a thin shell of any shape, and (v.) a certain family of screw-threads. It is doubtful whether there are any other possible types. Within these five types of symmetry the freehand method far surpasses analytical methods in its adaptability to boundaries and boundary conditions of almost any shape which can be drawn on paper. It possesses the further advantage of being tolerably rapid and free from the danger of large blunders. It can no doubt be extended to deal with conductivity which depends on position, on the potential, or on the force. The author hopes that it may be of use to designers of electric machinery.

Mr. A. RUSSELL said that electricians had often to draw lines of force freehand. As a rule they had little more than their intuition to guide them, as the values of many of the variables were only known roughly and the bounding-curves were not simple geometrical figures. They would therefore welcome the paper, as it would enable them to improve their diagrams. The problem of the flow in two-dimensional space could in many cases be satisfactorily solved by experiment—for instance, by Prof. Hele Shaw's method. The author had shown, however, that the graphical method could be applied usefully to certain classes of problems in three dimensions which it would be extremely difficult to attack by any other method. The speaker had found difficulty in determining the "chequer ratio" in electrical problems where the extent of the field was unlimited.

Mr. A. CAMPBELL asked if the author's method would be applicable to a helix of finite length carrying a current.

The CHAIRMAN remarked that in the method described much depended on the eye, judgment, and patience.

The AUTHOR, in reply to Mr. Campbell, said his method would not apply to the case of a helix of infinite length.

A paper by Dr. J. MORROW, "*On the Lateral Vibration of Bars supported at Two Points with One End Overhanging*," was read by the Secretary.

When a bar, supported at one end and at some other point in its length, vibrates under its own mass only, the expression from which the frequency can be determined is of considerable complexity. When different values are assumed for the ratio of the overhanging length to the distance between the supports, the expression reduces to a customary form with a co-efficient depending on this ratio. In the paper this coefficient is given to six figures for a number of different ratios from zero to unity. The results show that Dunkerley's approximate values cannot be relied on to more than two figures, and that Chree's simple formula gives remarkable accuracy for cases in which the overhanging length is less than half the span.

NOTICES OF BOOKS.

Text-book of Organic Chemistry for Medical Students. By Dr. G. v. BUNGE. Translated with Additions by R. H. ADERS PLIMMER, D.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

THESE lectures give an interesting account of the outlines of organic chemistry, paying special attention to the constitution and properties of those compounds with which the medical student should be thoroughly familiar, and laying stress upon their medicinal uses or physiological importance. The text-book has been greatly appreciated by German students, and there seems little doubt but that the freshness of its style and its conciseness will procure for it as ready a welcome in England as abroad. For the benefit of English students the translator has made some additions to Professor Bunge's work, and has inserted explanatory notes, and an appendix upon the usual methods of identification and estimation of the constituents of an organic compound, its purification, &c. The book is one which deserves great commendation, and medical students will find that they have every reason to be grateful to Professor Bunge for showing them what is in his opinion the most profitable way of studying organic chemistry.

Chapters on Papermaking. Vols. III. and IV. By CLAYTON BEADLE. London: Crosby Lockwood and Son. 1907.

THE form in which these chapters on papermaking are put before the public is distinctly novel, and presents some excellent features. The author set a number of practical questions, the object of which was to assist workmen to prepare themselves for the examination on papermaking by the City and Guilds of London Institute. These questions were answered by workers of all classes, and their written answers are reproduced and criticised here, with comments upon the mistakes which have been made, and suggestions by the author as to the correct and complete solutions. Many of the answers were written by working men, and nearly all show a considerable acquaintance with the practical aspects of the subject. For those who are unable to attend lectures upon papermaking the book represents the best possible substitute. Interest is awakened and held by the informal style, and the critical powers are called into action in the comparison of the various answers from which quotations are made; no better method could probably be devised to make the reader think and reason for himself, while the fact that incorrect replies are often quoted, and the mistakes explained, should help the student to get a thorough grasp of the ins and outs of the art of papermaking. In these two volumes fairly advanced questions are propounded, and each question is so worded that it almost invariably leaves considerable scope for a display both of the knowledge and reasoning power of the worker.

Nature's Hygiene and Sanitary Chemistry. By C. T. KINGZETT, F.I.C., F.C.S. Fifth Edition. London: Baillière, Tindall, and Cox. 1907.

THE reader who wishes to add to his knowledge of infection and sanitation will find that by the time he has read through this book he has acquired in a pleasant and easy fashion a good deal of miscellaneous information of interest and practical value, without having unduly taxed his mental powers in the process. At the same time it is well to warn him that the author's views are not always those generally accepted, even upon some questions which are no longer regarded as doubtful; thus he considers the ether to be non-existent, believing that there is no evidence of its existence. However, eccentricity in matters of scientific knowledge does not perhaps weigh very much against the author's sound common sense with regard to sanitary questions, or the value of his advice upon such practical subjects as the basis of disinfection and the treatment of the sick. The book gives a very readable account of the chemical and hygienic properties of eucalyptus, pine, and camphor forests, and lays special stress upon the merits of the Sanitas preparations which the author has put upon the market. The chemistry of the eucalyptus is fully treated, and the relations of micro-organisms to infectious and contagious diseases are discussed. The author does a useful work in urging the need of the appointment of chemical officers of health, to help and supplement the work of the medical officer.

The Repulsion Theory. By ARTHUR PERCIVAL KNIGHT. Los Angeles: Parker and Stone. 1907.

THE fundamental assumption in this treatise is that there is no action at a distance, or attractive action, but that all natural phenomena are due to mutually repulsive contact

actions of particles occupying space. The working out of the theory is based upon the kinetic theory of gases, and necessitates the assumption of the existence of a series of vortex systems. Thus the author regards the atom as a vortical unit, either non-rotative, as in the case of the elements of the zero group of the periodic system, or rotative, as in the case of the elements of Groups I. to VIII. of the system. The former atom is simple, and the latter either simple or complex; the atom may then be considered to be composed of subvortices, all of the same mass, that of the hydrogen equivalent. An attempt is made to demonstrate the unity of all forces, as different expressions of the repulsion due to impact, and of all forms of energy, but there are many weak points in the argument, which shows but little coherence and logical sequence, while some of the minor assumptions, such as that of valency, which is defined as the length of the axis of the atom measured in hydrogen equivalents, appear to be introduced merely for the sake of fitting in with the theory, and to show no connection with or dependence upon experimental facts or logical deductions therefrom.

The Commercial Possibilities of West Africa. By Viscount Mountmorres, F.L.S., F.R.G.S. Liverpool: The Offices of the Institute of Commercial Research in the Tropics. London: Williams and Norgate. 1907.

This paper has been reprinted for the Liverpool University Institute of Commercial Research in the Tropics, which is doing invaluable work in collecting and disseminating scientific information upon all subjects connected with the development of tropical countries. The paper, written by the Director of the Institute, was read at the Royal Colonial Institute, and gives an excellent account of the physiography of British West Africa; its mineral resources are enumerated, and a clear picture is given of the vastness of its forest wealth. As regards the ethnography of the country the Director speaks highly of the merits of some of the native races, and in conclusion he points out in what directions development is to be looked for in the not very far distant future.

Taschenbuch fur die Anorganisch-chemische Grossindustrie. ("Pocket-book for the Inorganic Chemical Industries"). By Prof. Dr. G. Lunge and Dr. E. Berl. Fourth Edition. Berlin: Julius Springer. 1907.

The last edition of Lunge's Pocket-book has been issued in a much enlarged form, and now instead of being devoted exclusively to the manufacture of soda, potash, and ammonia, it includes many other important industries, among which may be mentioned those of illuminating gas, calcium carbide, acetylene, manures, cement, &c. A useful compilation of numerical tables gives practically all the physical and chemical data which the analytical chemist would be likely to require, and a clear summary is added of the Patent Laws and the laws relating to trade marks of different countries. In the special part an account is given of the analysis of the raw materials and finished products of all the more important industries, in each case a single standard method of determination being described if possible; thus the chemist will have no difficulty or trouble in choosing between a number of methods, and he may feel confident that the processes given possess every advantage over those omitted in the way of rapidity and accuracy, and have, indeed, a claim to be regarded as the standard methods.

New Method of Forming Organic Compounds of Phosphorus.—Berthaud (*Bull. Soc. Chim.*, [4], i., 146) finds that when phosphorus is heated in a sealed tube with methyl alcohol at a temperature not below 250°, for several hours, the phosphorus disappears completely. The products are phosphoretted hydrogen and phosphines as gases, and as a residue phosphoric and phosphinic acids to some extent, but principally tetramethyl-phosphonium hydrate, $(CH_3)_2POH$.

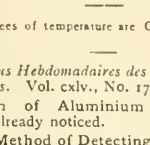
CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 17, October 21, 1907.

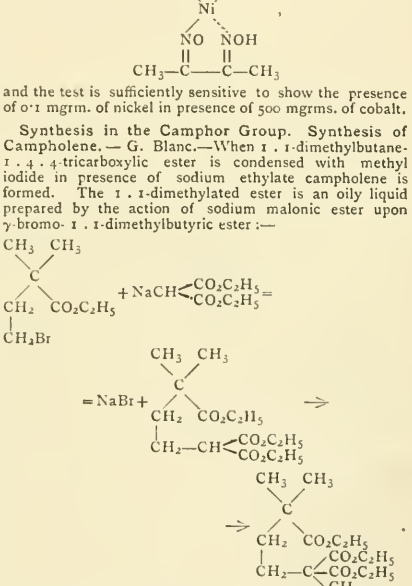
Preparation of Aluminium Carbide. — Camille Matignon.—Already noticed.

Sensitive Method of Detecting Nickel in presence of Cobalt.—Z. Tchougaeff.—Two years ago the author described (*Ber.*, xxxviii., p. 2520) the following method of detecting nickel in presence, not only of cobalt, but also of many other metals—such as magnesium, zinc, and cadmium. The method depends upon the formation of a bright red crystalline compound when dimethyl glyoxime, $CH_3{-}C{:}NOH{-}C{:}NOH{-}CH_3$, reacts with nickel salts in presence of ammonia. The formula of the red compound is—

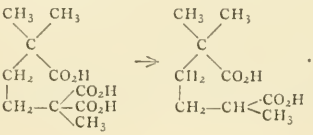


and the test is sufficiently sensitive to show the presence of 0·1 mgrm. of nickel in presence of 500 mgrms. of cobalt.

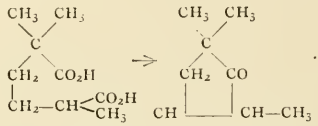
Synthesis in the Camphor Group. Synthesis of Campholene. — G. Blanc.—When 1 . 1-dimethylbutane-1 . 4 . 4-tricarboxylic ester is condensed with methyl iodide in presence of sodium ethylate campholene is formed. The 1 . 1-dimethylated ester is an oily liquid prepared by the action of sodium malonic ester upon γ-bromo- 1 . 1-dimethylbutyric ester:—



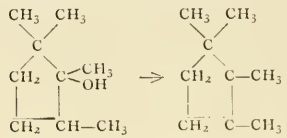
The corresponding acid, prepared by saponifying the ester with dilute potash, loses CO_2 at 205° and gives *aaδ*-trimethyladipic acid,—



and the latter can be converted by the action of acetic anhydride into an anhydride from which by distillation at the ordinary pressure 1 . 1 . 4-trimethylcyclopentanone-5 is obtained :—



This new ketone with methyl magnesium iodide gives a tertiary alcohol which loses water when distilled under ordinary pressure, and gives campholene :—



MISCELLANEOUS.

Society of Arts.—The programme of the arrangements for the new session of the Society of Arts has been issued, and is even fuller of interest than usual. A novel feature in it is the inclusion of a series of six lectures on Industrial Hygiene by different experts, who deal with such subjects as dust in factories and in mines, lead and mercury poisoning in pottery and match making, work in compressed air, and child labour. A course of lectures on the "Navigation of the Air" is to be given under the Shaw Trust by Dr. Hele Shaw. Four courses of Cantor Lectures are announced, the first on the Microscope, by Mr. Conrad Beck. There is a very full list of papers for the Ordinary and Sectional Meetings, and at Christmas Mr. Martin Duncan will lecture to a juvenile audience on the Cinematograph.

London Smoke : its Effect on Health.—The following is a summary of the proceedings at a Conference on this subject, held at the Institute of Hygiene, November 18th, 1907 :—

Sir William Richmond, who presided, said that experience goes to show that smoke is bad for the nervous system, bad for the bronchial tubes, bad for the eyes, and bad for the nose, but as he was not a doctor he preferred to speak of it so far as it affected himself, and its influence on works of art and decoration generally. The action of sulphuric acid present in smoke has an influence even upon marble, and will destroy copper-wire. The frescoes in the Houses of Parliament were destroyed, and much other damage could be chronicled through this cause. He quoted the late Sir William Broadbent as being a strong believer that smoke had a very bad effect on health, and he referred to the action successfully taken to save the plants at Kew Gardens, which, many of them delicate, suffer from smoke like human beings.

Dr. des Voeux said he would move the following resolution :—

> "That the coal-smoke in the atmosphere is injurious to health and lowering to vitality, and that every possible means should be adopted to find a remedy."

He described the chemical constituents of smoke, and asked what are the deleterious constituents? He said that he believed these were the sulphurous compounds. The carbon was carried into the lungs, but he did not think this did any harm—the sulphurous compounds were, however, very irritating. Dr. Ascher, a German doctor, had made a very close study of this subject, and he found that disease and mortality were greater nearer to factories and where there was much smoke, and he proved beyond a doubt that human vitality was much less when living under the influence of smoke. Smoke produced many troubles, including indigestion and catarrh of the stomach, and its worst effect was when smoke was in combination with fog. He thought the indirect effect on health was, however, even greater than its direct effects, and while he was anxious not to overstate the case he certainly thought it seriously impaired health.

Mr. Chubb dealt also with the chemical effects, and suggested the burning of smokeless fuel.

Mr. Baines said the difficulty was to find a practical remedy, and he hoped this would be proposed at the meeting.

Other speakers having stated their views the resolution was put to the meeting and carried unanimously.

MEETINGS FOR THE WEEK.

Monday, 25th.—Society of Arts, 8. (Cantor Lectures). "Theory of the Microscope," by Conrad Beck, F.R.M.S.

Wednesday, 27th.—Society of Arts, 8. "The Franco-British Exhibition, 1908," by the Hon. Sir John A. Cockburn, K.C.M.G.

Friday, 29th.—Society of Arts, 8. (Shaw Lectures on Industrial Hygiene). "The Hygiene of Work in Compressed Air (Diving, Caisson Work, Sub-aqueous Tunnelling, &c.)," by John Scott Haldane, M.A., F.R.S., &c.

Re THE SCOTTISH CYANIDE CO., Ltd.
(IN LIQUIDATION).

On WEDNESDAY, 18th, and THURSDAY, 19th DECEMBER, 1907,
At THE KIRKLAND WORKS, LEVEN, FIFESHIRE,
HIGHLY IMPORTANT and EXTENSIVE SALE of

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FOUR SETS of WILLIAMS and ROBINSON "3T" TRIPLE-EXPANSION ENGINES, with EIGHT MATHER and PLATT LOW-TENSION ALTERNATORS. Each Engine is capable of giving out 800 H.P. with 160 lbs. steam pressure.
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FIFTEEN ELECTRIC FURNACES;
TWO LARGE DOWSON GAS PRODUCERS, with Blowers;
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THE CHEMICAL NEWS.

Vol. XCVI., No. 2505.

NOTE ON THE ASSOCIATION OF HELIUM AND THORIUM IN MINERALS.*

By the Hon. R. J. STRUTT, F.R.S.

The question has been often raised of whether or not helium is a product of thorium radio-activity. My own view throughout has been that it is (*Proc. Roy. Soc.*, 1904, lxxiii., 191; also March 2, 1905). Mr. Boltwood has recently argued that the helium in radio-active minerals may always be attributed to the action of the uranium-radium series of transformations (*Am. Journ. Sci.*, February, 1907, xxiii., 77). I wish in the present note to draw attention to a case where that view is clearly untenable.

Prof. Julius Thomsen, of Copenhagen, described, in 1898 (*Zeit. Physikalische Chemie*, xxv., Part 3), a helium mineral from Ivitgut, Greenland, similar in some respects to fluor-spar, but containing rare earths. Recently he has determined the quantity of helium liberated on heating as 27 cc. per kilogrm. (*Bull. de l'Acad. Royale des Sciences, Copenhagen*, 1904, 53—57).

Prof. Thomsen kindly sent me a supply of this mineral. I have carefully tested it for radium, and find that it contains no more than the traces which are ubiquitous in rocks and minerals. The quantity found was, in fact, about the same as in average rocks, and is insufficient to account for one-hundredth part of the helium present.

On the other hand, a solution of the mineral gave abundant thorium emanation. I am inclined to think that there is some unknown complication about the thorium-emanating power of solutions which makes it unsafe, in certain cases at least, to infer from it the quantity of thorium present. But enough thorium emanation was given off by the solution to show that thorium was a substantial constituent of the mineral. I regard it as entirely certain that the helium in this mineral has not been generated *in situ* by uranium or radium, and have no hesitation in connecting it with the presence of thorium.

A WATER-JET BLOWER OF VERY SIMPLE CONSTRUCTION.

By S. M. REVINGTON and I. G. RANKIN.

The blowing apparatus at present used generally consists of a copper cylinder with metal filter-pump attachment, together with gauges, &c., the cost being about 15s., and the efficiency far from excellent.

We wish to describe an apparatus we have set up for the purpose whose cost is practically nil, and which requires no skill in its manufacture.

A large bottle, say of 4 litres capacity, is fitted with a good cork pierced with holes for four tubes whose diameters are:—(A) ¼, (B) ¼, (C) ⅛, and (D) ¼ inch.

The tube A has a somewhat sudden constriction made in it. Into the upper end of this tube the jet delivers in such a way that it goes diagonally across the tube on to the side of the constricted part. We found experimentally that such a direction seems to give the best results.

It is this modification of the usual filter-pump attachment that has rendered the blower really efficient.

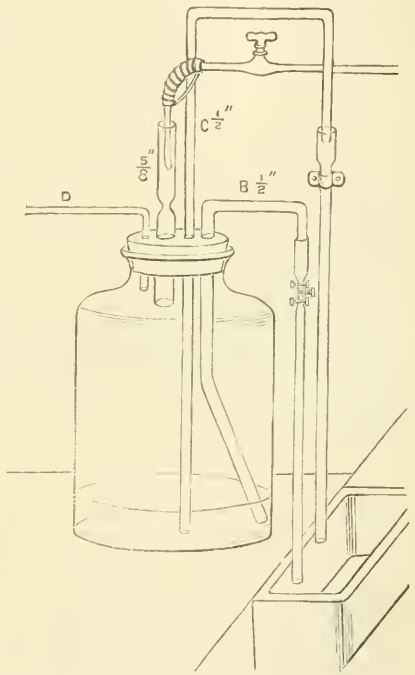
The tube B is a syphon outlet consisting of a wide bent tube passing to the bottom of the bottle and connected at the other end to similar bore tube discharging into the sink. A clip is attached to the rubber to regulate the outfall.

The tube C is a safety tube, not quite reaching the bottom of the bottle and about 2 ft. 6 in. in height, bending at the top so as to discharge into a wide tube leading to the sink.

Air passes out of the tube D, which just passes below the cork.

When the water is turned on and the air exit kept closed, as may be done by a blowpipe with air control, the pressure first starts the syphon, and afterwards air and water escape by the safety, so that the pressure quickly reaches a maximum.

On now releasing the blast, it will be found sufficient for the full gas and to work very steadily. During the course



of our present work we have joined ¼-inch Jena tube and blown 300 cc. bulbs by its aid, and found it far superior for use with a small blowpipe to blowing with the mouth in the case of joining up long pieces of apparatus.

A platinum crucible can be kept white hot for any length of time, which is a great advantage in such cases as the ignition of $CaCO_3$ to CaO.

By blowing a tube into the side of A and connecting the jet to A with rubber tubing, the arrangement being similar to that of the head of a filter-pump, the apparatus can be employed for circulating gas when it is required to do so in large quantity.

With regard to details the position of the jet may be adjusted by noting the height of water in the safety tube, while the same holds in the case of controlling the

* A Paper read before the Royal Society, November 7, 1907.

outfall by means of the clip, care being taken that the bottle does not begin to fill. Under these conditions the amount of water used is about that taken by an ordinary Bunsen filter-pump.

It is as well also to varnish or cement the cork to preserve it and to prevent leakage of air, though the latter, if slight, is immaterial.

In conclusion, we may add that several other blowers which have since been set up in the chemical laboratories of University College have proved quite as satisfactory as our own.

MANGANESE AND THE PERIODIC LAW.

By H. REYNOLDS, B.Sc., Ph.D.

In most charts of the periodic classification of the elements the following arrangement is adopted:—

VI.	VII.	VIII.			o.	I.
S	Cl				Ar	K
Cr	Mn	Fe	Ni	Co		Cu
Se	Br				Kr	Rb
Mo	—	Ru	Rh	Pd		Ag
Te	I				Xe	Cs
	—					
W	—	Os	Ir	Pt		Au

This arrangement is based on the facts that, unless Mn were placed in the VII.th group, this group would contain only one column of elements, and that $KMnO_4$ happens to have a similar formula to $KClO_4$ and to share with it the property of being an oxidising agent.

On the other hand, the to-be-expected homologues of Mn, metals to come between Mo and Ru and between W and Os, have not yet been discovered, and there is only the slightest reason for supposing such metals to exist. Further, Mn, in both its physical and chemical properties, shows the closest resemblance to the metals of the iron group, whereas it shows practically none to the halogens. Potassium manganate is not even similarly constituted to potassium chlorate.

A much better arrangement is to place Mn in the VIII.th group, which will then be—

Mn	Fe	Ni	Co
Ru	Rh	Pd	
Os	Ir	Pt	

This arrangement gives expression to the facts that Mn, Fe, Ni, Co are metals of similar appearance, mechanical properties, specific gravity, and melting-point; that their divalent simple and double salts are similarly constituted and isomorphous, *e.g.*, $MeSO_4,7H_2O$, $R_2SO_4MeSO_4,6H_2O$, &c.; that Mn, Fe, and Co all form alums and metallo- and metallicyanides. Mn shares this last property with Ru and Os, and its most highly oxidised salts, K_2MnO_4 and $KMnO_4$, are paralleled by K_2RuO_4, $KRuO_4$, and K_2OsO_4.

Further, a fuller examination of the properties of the metals of this group shows in many cases a regular gradation from Mn to Co in the top line and a corresponding gradation from Ru to Pd and from Os to Pt.

It is not necessary to assume the existence of a series of at present unknown elements to fill the vacant column in the VII.th group. This group is not alone in having only a single column of elements; the argon group bears it company in this respect.

The Chemical Laboratory,
L.C C. Paddington Technical Institute,
Saltram Crescent, W.

THE TECHNICAL DETERMINATION OF BENZENE IN ILLUMINATING GAS.

By D. A. MORTON.

The value of benzene vapour as a light producer in illuminating gas has led to its extensive use for enriching purposes, and its exact estimation in a simple way has become a matter of consequence.

Since 1 per cent only in coke oven gas gives a lighting value of more than twelve candle-power, while 1 per cent of ethylene gives less than one and one-half candle-power, there is a large difference in the lighting value of these constituents and their separate determination is necessary.

Although a number of methods have been proposed for the determination of benzene, and some of these requiring long and careful manipulation are quite exact, none appears to be satisfactory for use in technical work where a simple and rapid, as well as reasonably accurate, test is desired.

W. Misteli (*Journ. Gasbeleucht*, Sept. 9, 1905, p. 804), in a recent review, cites the method of Haber and Oechelhaeuser (*Ber.*, xxix., 2700) as being the only one suitable for testing small quantities of gas, yet even this method does not compare in rapidity and simplicity with the ordinary volumetric tests in technical analyses. The gist of the method is the absorption of the ethylene by bromine water and subsequent titration of the excess of bromine. Benzene vapours, the authors claim, while dissolving completely or partially in the bromine water, do not unite chemically with the bromine and hence do not affect the titration. Only by long contact is there a slight reaction with the benzene. The difference between the ethylene found and the total illuminants is taken as the percentage of benzene.

The method of Dennis and O'Neill, published in 1903 (*Journ. Am. Chem Soc.*, 1903, xxv., 503), in which the benzene vapours are absorbed by shaking the gas in a pipette with ammonium nickel nitrate solution of prescribed strength, is, unlike the preceding method, simple and rapid and suitable in these respects for technical use. The nickel method was used for a considerable time in this laboratory because, on account of its convenience and supposed accuracy, it was presumed to be suitable for the purposes here required. Nevertheless on a number of occasions the tests were found to be incorrect and consequently a more exhaustive investigation of its merits was finally carried out, with results of such interest that we give them in detail below.

Investigation of the Ammonium-nickel Nitrate Method.

The ammonium-nickel nitrate solutions for the experiments were made up according to the directions given in the original article (*loc. cit.*, p. 505). Both the regular solution and Geer's solution were tried, with identical results; and, since the solutions were made up by more than one analyst and at a number of different times, we cannot suppose the errors found in the tests to have been due to errors in preparing the solutions.

Following the directions of the authors in carrying out the tests, mixtures of benzene vapour and air were analysed, 100 cc. of the gas mixture being shaken three minutes in an absorption pipette with the ammonium-nickel nitrate solution, then three minutes in a second pipette with 5 cc. of 5 per cent sulphuric acid over mercury to remove ammonia fumes. The decrease in volume by this treatment indicates the percentage of benzene.

Table A shows the results obtained. The percentage of benzene present in each case was determined by absorption with fuming sulphuric acid as in the regular way for illuminants. Besides the percentage of benzene present, and that found by the ammonium-nickel nitrate test, the table gives the cubic centimetres of benzene vapour previously absorbed by the reagent, for this has a decided influence, as will appear.

A glance at the results of Table A shows that the absorbing solutions must be perfectly fresh to obtain results that are even approximately correct. In tests 2 to 6, although at most only a small quantity of benzene vapour had previously been absorbed, in no case has more than three-fourths the benzene actually present been found by the test. In 1, 100 cc. of air, shaken with the reagent and the 5 per cent sulphuric acid, has its volume *increased* to 101·1 cc.

If fresh ammonium-nickel nitrate solution and fresh 5 per cent sulphuric acid are used for each test (7 to 10) the results are better, though still too low by several tenths of 1 per cent. In technical works, where complete analyses have sometimes to be made as frequently as once an hour, refilling the pipettes with fresh solutions for every test is an inconvenience that is best avoided. An improvement has been made in the laboratory of the Detroit Solvay works, where the gas mixture is shaken three minutes in each of two ammonium-nickel nitrate pipettes, thus keeping the contents of the second pipette comparatively fresh for some time.

On further examination we find not only that the ammonium-nickel nitrate solution is an indifferent absorbent for benzene, but also that the absorbing power it does possess is due, *not to the nickel compound but to the water present*. That either water alone or dilute aqua ammonia gives practically the same results as the ammonium-nickel nitrate solution is shown in the table of comparative tests (Table B).

Table B shows results from a number of tests made under conditions as nearly identical as possible in all comparative cases. In I. fresh absorbing solutions were used. The gas taken for the test was air containing benzene vapour. One hundred cc. of the gas were passed into the absorbing pipette and shaken with the absorbent for the number of minutes indicated, drawn out and passed into a pipette of 5 per cent sulphuric acid to remove fumes, then back into the burette, allowed the usual time to drain, and measured. In II. the same conditions were observed except that the absorbing solutions were not fresh, having been used for the tests under I. In III. the gas in each case was shaken with the fresh reagent three minutes, then with 5 per cent sulphuric acid three minutes, the tests all being made with especial care.

Table C shows the results of strictly comparative tests of the absorbing power of ammonium-nickel nitrate solutions and pure water. In each case exactly 118 cc. of the absorbing solution were shaken for the time stated with 100 cc. of the gas and the unabsorbed residue drawn slowly back into the burette and measured. The gas was drawn back slowly to insure complete absorption of all ammonia fumes. (One hundred cc. of air passed into the fresh ammonium-nickel nitrate solution, shaken one minute and drawn back in the same way, re-measured exactly 100 cc.) Temperatures were the same, 18—19°, in all instances. In each case the gas tested was a mixture of air and a known quantity of benzene vapour.

From the results given in Table B we can draw no other conclusion than that in the determination by ammonium-nickel nitrate solution the benzene vapour is simply dissolved to a certain extent by the water in the solution—perhaps increased slightly by the ammonia in the case of the high percentages—but that the presence of the nickel compound has no appreciable influence whatever.

It would answer better to simply use fresh water each time as the solution for absorbing benzene, and, if used under proper conditions, good results could perhaps be obtained with this reagent. Nevertheless the use of a fresh solution, even water, for every test involves certain inconveniences and liabilities to error and would be objectionable in technical practice.

By the use of concentrated sulphuric acid for the benzene absorption a better method is obtained. This method is reliable and convenient, and the results by it are so comparatively accurate that we have no hesitation in recommending it for the technical analysis of coal gases.

TABLE A.

	Benzene present. Per cent.	Benzene found. Per cent.	Benzene vapour previously absorbed. Cc.
1.	0·0	−1·1	17
2.	0·5	0·0	17
3.	0·6	0·1	17
4.	0·6	0·3	1
5.	4·3	3·3	8
6.	4·7	3·2	12
7.	0·5	0·35	0
8.	1·0	0·7	0
9.	1·8	1·4	0
10.	4·2	3·7	0

TABLE B.

Absorbing solution.	Minutes shaken.	Benzene present. Per cent.	Benzene found. Per cent.	Benzene vapour previously absorbed. Cc.
I.				
Ammonium-nickel nitrate	3	9·9	9·0	0
Aqua ammonia (sp. gr. 0·95)	2	9·9	8·8	0
Water	3	9·5	8·1	0
II.				
Ammonium-nickel nitrate	3	9·9	8·0	9·0
Aqua ammonia (sp. gr. 0·95)	3	9·9	8·2	8·8
Water	3	8·4	7·4	8·1

III.

No. of test.	Benzene present. Per cent.	Benzene by ammonium-nickel nitrate. Per cent.	Benzene by water. Per cent.
1.	0·5	0·35	0·4
2.	1·0	0·7	0·8
3.	1·8	1·4	1·5
4.	4·15	3·65	3·4
5.	3·95	—	3·5
6.	4·15	3·6	3·35

TABLE C.

Series.	Absorbing solution.	Minutes shaken.	Benzene found. Per cent.	Benzene present. Per cent.	Benzene previously absorbed. Cc.
I.	Ammonium-nickel nitrate	2	6·1	7·2	0
	Water	2	6·0	7·2	0
II.	Ammonium-nickel nitrate	3	2·3	3·6	6
	Water	3	2·3	3·6	6
III.	Ammonium-nickel nitrate	2	0·4	1·0	0
	Water	2	0·4	1·0	0

TABLE D.—*Benzene-air Mixtures.*

No. of test.	Benzene present. Per cent.	Benzene found. Per cent.
1.	0·5	0·5
2.	0·6	0·6
3.	0·65	0·6
4.	1·9	1·9
5.	3·0	3·1
6.	3·6	3·55
7.	4·0	3·8
8.	4·5	4·35
9.	4·7	4·6
10.	7·8	7·7

TABLE E.—*Benzene-air Mixtures.*

No. of test.	Gas tested.	Benzene vapour previously absorbed.	Benzene present.	Benzene found
		Cc.	Per cent.	Per cent.
1.	Benzene-air ..	55	1·9	1·9
2.	,, ..	120	3·0	3·1
3.	,, ..	150	4·5	4·3
4.	Air	55	0·0	0·0
5.	,, ...	100	0·0	0·0

TABLE F.—*Benzene-ethylene-air Mixture.*

No. of test.	Benzene present.	Benzene found.	Ethylene present.	Ethylene found.
	Per cent.	Per cent.	Per cent.	Per cent.
1.	0·55	0·85	9·5	9·5
2.	0·50	0·70	10·1	10·0
3.	0·50	0·65	4·8	4·7
4.	0·50	0·60	5·0	4·8
5.	1·0	1·05	9·95	10·1
6.	1·0	1·0	4·8	4·8
7.	1·0	1·05	5·0	5·0
8.	2·85	2·85	4·4	4·6
9.	3·0	3·0	4·5	4·7

TABLE G.—*Cubic Centimetres Ethylene Absorbed in Benzene Test.*

Ethylene present.	Benzene present (per cent).		
	0·0.	0·5.	1·0.
Per cent.	Cc.	Cc.	Cc.
1	0·05	0·00	0·00
2	0·10	0·05	0·00
3	0·10	0·05	0·00
4	0·15	0·10	0·05
5	0·20	0·10	0·05
6	0·25	0·15	0·10

The Concentrated Sulphuric Acid Method.

The marked solubility of benzene vapour in water (see Tables B and C) renders necessary certain precautions in sampling and handling the gas previous to the test. If taken over water, the sample bottle should be completely filled with the gas, driving out practically all of the water, as otherwise some of the benzene will be absorbed.

After the determination of the carbon dioxide in the gas, by absorption in strong caustic soda or potash solution in the usual manner, the benzene test is accomplished as follows. (Caustic soda solution dissolves benzene to only a very slight extent, and the error caused thereby is negligible).

The gas residue is passed into an ordinary simple absorption pipette containing concentrated sulphuric acid (sp. gr. 1·84) and shaken *vigorously* with this reagent for one minute, by which treatment the benzene vapours are absorbed. (Slight dilution of this acid does not detract from its efficiency, but the dilution should not exceed 2 per cent). The shaking is satisfactorily accomplished by giving a quick sharp motion to the pipette in such a way as to mix the contents thoroughly about twice per second, during the specified one minute. It is essential to shake vigorously with the sulphuric acid as directed, for the last traces of benzene are absorbed slowly and require thorough contact with the acid.

Experimental data on the conduct of concentrated sulphuric acid as an absorbent for benzene are given in Tables D to G.

Table D shows results obtained with mixtures of benzene and air. Good results are obtained even when more than 7 per cent of benzene—a very high amount—is present.

Table E gives results showing that the concentrated sulphuric acid can be used for a large number of tests without renewal. The benzene combines with the sulphuric acid and is not removed by air subsequently introduced.

Table F shows the action of concentrated sulphuric acid on benzene-ethylene-air mixtures. The benzene is determined by the concentrated sulphuric acid test; the ethylene immediately afterwards by fuming sulphuric acid in the usual way. In this table a slight defect in the method appears, due to the absorption of a trace of ethylene by the concentrated sulphuric acid. Higher homologues of ethylene would be absorbed to a greater extent than ethylene itself. The error diminishes rapidly as the percentage of benzene increases, becoming practically nil when 1 per cent or more of the latter is present, and probably not exceeding 0·2 per cent in the case of any coal-gas.

Table G shows the cubic centimetres of ethylene absorbed by the concentrated sulphuric acid test, per 100 cc. of gas, having given the percentage of benzene and ethylene present. By use of these data correction for the error can be made when desirable.

Conclusions.

From the results obtained the unsatisfactory character of the ammonium-nickel nitrate method is apparent. As pure water absorbs benzene to practically the same extent as the ammonium-nickel nitrate solution, it appears that the method really depends on the solubility of benzene vapour in water, or ammoniated water, and that the presence of the nickel compound has no influence. The results by the method are inaccurate and vary widely according to the amount of benzene in the gas and the quantity already present in the absorbing solution.

Concentrated sulphuric acid, on the other hand, absorbs benzene vapour as readily as could be desired, and can be used for a large number of tests without renewal, giving as accurate results after a hundred tests as when first prepared. The defect due to the absorption of ethylene is insignificant, but may be easily corrected for (see Table G). Traces of the higher olefines, however, may give a value slightly too high for the benzene percentage, though this error, as shown by our tests of rich and lean gases from a variety of coals, must be small, if not inappreciable.—*Journal of the American Chemical Society*, xxviii., No. 12.

OBSERVATIONS ON THE

YELLOW MODIFICATION OF MOLYBDIC ACID.

By JOHN HOWARD GRAHAM.

INVESTIGATIONS have shown that the yellow crystalline substance depositing from solutions of ammonium molybdate is of composition $H_2MoO_4.H_2O$. It was noticed as early as 1876, identified in 1882, and a crystal measurement made in 1903. The following is an extract from the paper as presented.—ED. *Journ. Franklin Institute.*

Recently, while transferring ammonium molybdate solution from a stock bottle to smaller reagent bottles, I noticed on the bottom of the former a yellow crystalline incrustation, and there were some loose crystals. There is scarcely a chemist who has not noticed a yellow, yellowish white, or white deposit under similar conditions; but I have never observed one so uniformly yellow and homogeneous, and my curiosity led me to the following investigation, the results of which, I think, should prove of interest to everyone handling such solutions.

I removed as much of the crust as I could, crushed it carefully, so as to expose the individual crystals, and then washed with pure water to remove adhering solution. The material was then air-dried. Whenever I had noticed the deposits from solutions of ammonium molybdate, without any good reasons for my doing so, I considered them basic

or acid ammonium molybdates, that is, salts in which either ammonia or molybdic acid predominates. With such views in mind, qualitative tests were made with the following results :—

The yellow substance is very sparingly soluble in water, and the aqueous solution decomposes on concentration, affording a bulky white precipitate, very soluble in ammonia, and this ammoniacal solution deposits on evaporation white crystals of the molybdates of ammonia, several because as many kinds of crystals were observed. The white precipitate is undoubtedly molybdic anhydride. Another sample of our material was found insoluble in nitric acid, as might be suspected from the fact that it deposits after continuous standing from solutions strongly acidified with nitric acid. The aqueous solution is decomposed by nitric acid, giving the same milky-white precipitate which I consider molybdic anhydride. It is very soluble in hydrochloric acid, in fact excessively so, making the solution syrupy. Heated very gently, it yields water ; at a higher temperature it turns bluish in colour, and if the heating is continued without air access, it becomes yellow and finally white when cold, and shows indications of incipient sublimation. When heated to redness it sublimes completely, the sublimate having all the appearances of pure molybdic anhydride. The results so far could easily have been obtained with any ammonium molybdate. The question suggested itself :—Does it contain any ammonia ? A rather large sample of the material was boiled with strong caustic soda. I thought I noticed ammonia. Test paper impregnated with mercurous nitrate solution just turned faintly brown. My conclusions were, that if the substance was a molybdate, it must be of a very acid character. Examined under the objective of a microscope magnifying 85 diameters, the crystals appeared clear, well-defined, and prismatic. They were so small that I could not make out whether they were of the isometric or the monoclinic system. Later, I obtained larger crystals, and upon examining them, placed them in the monoclinic system.

With the foregoing facts in hand, literature was searched with the hope that light would be thrown upon the subject. We looked up molybdates, of course, and found nothing that would agree with our substance even qualitatively. A great number of molybdates of ammonia were described by Kämmerer (*Journ. Prakt. Chem.*, 1850, Series 1, xlix., 445) and Delafontaine (*Journ. Prakt. Chem.*, 1865, Series 2, xcv., 136), the information in many cases being meagre and uncertain. It might be of interest to note that Kämmerer estimated molybdic anhydride by reducing with hydrogen to constant weight, and weighing the molybdenum dioxide ; also by heating the salt with air access, adding drops of hydrochloric acid from time to time, and finally weighing the molybdic anhydride. The ammonia was determined by the well-known soda-lime method, the evolved gas being collected in hydrochloric acid, and finally weighed as platinum.

The next most logical proceeding was to determine the composition of the substance by estimating water, molybdic anhydride, and ammonia. The method used by Kämmerer, and suggested by Fresenius, that of reduction by hydrogen, was used. Fresenius says, to use a porcelain boat in a hard glass tube, and that the temperature should not exceed a dull redness. I tried this. The water of crystallisation passed over at a very low temperature, and, unless this is increased, no more water comes over. Heating to a dull redness, water resulting from the reduction of the molybdic oxide passes over. At the end of about two hours, the reaction has ceased. The material has suffered various changes of colour, yellow to orange, to blue, to black, and to steel-grey.

Rammelsberg states that the contents of the crucible are frequently grey below and brown above (*Pogg. Ann.*, cxxvii., 281 ; *Zeit. Anal. Chem.*, v., 203). What I obtained was uniformly grey, and the weighings of the supposed molybdenum dioxide gave percentages of molybdenum trioxide as follows :—60·97, 61·12, 60·53, 61·55, 61·95, 61·82, 61·02, 61·64.

Having taken all proper precautions, yet the results were anything but concordant. My attention was next given to the ammonia content. Samples of 1 grm. of material each were thoroughly mixed with finely-divided soda-lime, and heated in the usual combustion tube for that purpose. The ammonia was collected in hydrochloric acid, and was to have been determined as platinum. From two determinations I obtained such slight traces of the double chloride of platinum and ammonium that I had to consider the ammonia as a negligible trace. I was greatly surprised. I attributed the traces of ammonia to ammonium nitrate occluded in the crystals, and made the ferrous sulphate and diphenylamine tests for nitric acid. The former was altogether unsuccessful, for the former salt immediately reduced the solution and gave the intense blue due to the lower oxides of molybdenum. With the other reagent I first obtained a blue, due, I think, to nitrates, and after a time the solution became intensely blue, due again, I think, to reduction of the tri-oxide of molybdenum. Undoubtedly the ammonia is present in small traces as nitrate. So my yellow substance contains no ammonia in its composition. This directs me upon a new course. As to the water content, two samples of material heated in covered porcelain crucibles, with flames about one inch high and barely touching the bottom, gave results as follows by difference :—20·07 per cent and 20·03 per cent.

The ammonium molybdate solution from which the material was deposited was purchased from Baker and Adamson and guaranteed pure. There could be present in the yellow substance, therefore, no base but ammonia, and no acids other than nitric and molybdic acids. Since ammonia and nitric acid are present only in traces, we can consider them out of the question. The material therefore should contain nothing but molybdic acid and water, both of which were found and estimated. If the water is present by 20 per cent, there should be 80 per cent of molybdic anhydride. How shall we account for the discrepancy between 61 per cent about, as determined, and 80 per cent theoretical ? It could be possible that the contents of the boat were overheated. The supposed molybdenum dioxide did look too grey when compared with the colour by which it has been described—brown to black. It looked exactly like the metal molybdenum itself, and it is possible to obtain the metal under these conditions. In order to see if I could get a different result by regulating the temperature more carefully, I heated a sample by stages, intending to stop the operation when I obtained constant weight. With a very low flame I obtained a result which, calculated for molybdic anhydride, gave 85·05 per cent. The height of the flame was then increased so as to have it just touch the tube. The percentage dropped to 78·77. Evidently the crucial point was again overstepped. The following three determinations were made with the flame not quite touching the tube—a Bunsen flame of about 1½ inches. The contents of the boat after cooling were uniformly dull black and homogeneous throughout.

Result.—79·93 per cent, 79·73 per cent, 80·00 per cent, the mean of which is 79·93 per cent, and this added to the mean of the water determinations, 20·05 per cent, gives 99·93 per cent, corresponding to the formula $MoO_3.2H_2O$ or $H_2MoO_4.H_2O$.

References to this substance are few, yet they furnish substantially what I have enumerated above. I did not conceive of the substance being a modification of molybdic acid or I should have discovered earlier that the ground had practically been covered by others.

In the year 1876 Junck observed the yellow deposit. (*Zeit. Anal. Chem.*, xv., 290). He thought it was a metameric form of molybdic acid resulting from the action of light upon the solution. He made several experiments along this line.

Sergius Kern took notice of the deposit, and published notes concerning it in 1878 (*Zeit. Anal. Chem.*, xvi., 52).

In 1882 Millingk makes mention that the yellow precipitate is $MoO_3.2H_2O$, and gives a meagre description,

adding that it is soluble 0·5 grm. about in 1 litre of water (Gmelin-Kraut's "Handbuch," 1882, [2], II.).

Parmentier, 1882, makes quite a thorough study of it, and his observations as to its physical and chemical properties and composition agree quite closely with mine (*Comptes Rendus*, 1882, 839). The results of his analyses are :—

H_2O	19·96	19·95	19·94
MoO_3	80·04	80·05	80·06

Parmentier mentions that the crystals are monoclinic in form, and in 1888 Vivier confirmed this statement (*Comptes Rendus*, 1888, cvi., 601).

It was not until 1903 that the final work upon the substance was done. De Schulten (*Bulletin French Min. Soc.*, 1903, xxxvi.) prepared the yellow material according to the methods of Parmentier, acknowledging and confirming all his statements. He puts his solutions aside for years so as to obtain crystals large enough for measurement, and when he obtained some measuring 0·9 mm., 0·8 mm., and 0·8 mm. respectively along the axes *a*, *b*, and *c*, he uses them for this purpose. In his paper reporting the work, he makes a drawing of one of the crystals, which shows the following forms :—

Positive and negative pyramids and orthodomes; two prisms, clino-dome, ortho- and clino-pinacoids, and basal plane. The angle between the basal plane and the ortho-pinacoid is 89·19°, making the crystals appear at first glance as though they were cubes. They are clear, and the faces are good reflectors.

Yellow molybdic acid is so far an unimportant substance, a mere chemical curiosity, but yet its manner of formation and its occurrence are of interest, and it deserves that we know its properties sufficiently well to be able to identify it. —*Journal of the Franklin Institute*, clxiii., No. 1.

A NECESSARY MODIFICATION OF VOLHARD'S METHOD FOR THE DETERMINATION OF CHLORIDES.*

By M. A. ROSANOFF and ARTHUR. E. HILL.

1. *On the Determination of Chlorides.*

VOLHARD'S method for the determination of chlorides is well known. It consists in acidifying the given solution with nitric acid, adding a ferric salt (say iron-ammonium alum) as an indicator, precipitating the chloride with a measured but excessive amount of a standard silver nitrate solution, and without filtering out the silver chloride, determining the excess of silver nitrate by titration with a standard solution of ammonium sulphocyanate. As long as the solution contains any silver, the ammonium sulphocyanate produces only a white precipitate of silver sulphocyanate. When the silver is gone, the solution is coloured red by the sulphocyanate of iron.

A somewhat extensive experience in using this rapid method gradually forced upon us the feeling that in its present form it is inaccurate. The more carefully the titration is carried out, the less distinct the end-point often seems to be. A historical investigation showed that others have had similar experience with the method. Some time after the appearance of Volhard's first paper (*Journ. Prakt. Chem.*, 1874, ix., 217) Brügelmann reported (*Zeit. Anal. Chem.*, 1877, xvi., 1) that the end-point in question was indistinct, explaining it, however, on the assumption that it was the free nitric acid present that was destroying the colour by oxidising the sulphocyanate. The interfering factor was more clearly discerned by Drechsel (*Journ. Prakt. Chem.*, 1877, xv., 191 ; *Zeit. Anal. Chem.*, 1877, xvi., 351), who found that sulphocyanate of iron is decomposed by the silver chloride first precipitated according to the following equation : $Fe(CNS)_3 + 3AgCl = FeCl_3 + 3AgCNS$. He consequently recommended filtering out the silver chloride before titrating with sulphocyanate. Then appeared Volhard's exhaustive and final paper on the determination of silver and the halogens (*Liebig's Ann.*, 1878, clc., 8). Volhard, on the one hand, refutes Brügelmann's view and, on the other hand, maintains that the decomposition of dissolved sulphocyanates by solid silver chloride, pointed out by Drechsel, is too slow to interfere with the precision of the method. "Since," he says, "as mentioned, the decomposition of silver chloride by sulphocyanic acid or by a solution of ammonium sulphocyanate proceeds *quite slowly*, a liquid faintly coloured by iron sulphocyanate is but very gradually decolorised by silver chloride. . . . This renders it possible to determine, by means of sulphocyanate, the quantity of silver contained in a nitric acid solution in the presence as in the absence of silver chloride." Nevertheless, he urges extreme caution in looking for the end-point, that is, for the first appearance of a permanent coloration ; for he had found that in the presence of some 0·4 grm. silver chloride the very faint light-brown coloration first produced by the sulphocyanate failed to be intensified by the addition of eight more drops, accompanied by thorough shaking.

At present, analysts are not in agreement as to whether the precipitated silver chloride interferes or not with the sulphocyanate titration. Thus, to Sutton "experience has proved that it is absolutely necessary to filter off the chloride and titrate the filtrate and washings" ("Volumetric Analysis," Philadelphia, 1904, footnote to p. 144). Similarly, in connection with a precise physico-chemical study Knüpffer found it necessary to filter off the silver chloride ("Chemisches Gleichgewicht und Elektromotorische Kraft" in *Zeit. Phys. Chem.*, 1898, xxvi., 266). He believes, however, that the action of silver chloride on sulphocyanates is "very slight" and that removing the chloride is necessary only in case of highly dilute solutions. *But the majority of chemists consider the removal of the chloride unnecessary in any case.* Thus, Treadwell ("Analytische Chemie," vol. ii., p. 510, Leipzig and Vienna, 1905) makes no mention at all of any possible interference by the silver chloride, nor does the United States Pharmacopœia refer to it. Mohr and Classen ("Lehrbuch der Chemische-analytischen Titrimethode," Braunschweig, 1886, p. 403) state explicitly that the removal of the chloride is unnecessary and recommend Volhard's method in its original form. Finally, to quote one more authority, Friedheim directs ("Leitfaden für Quantitative Chemische Analyse," Berlin, 1897, p. 125) " . . . And now, without filtering off the silver chloride, or even taking pains to cause it to coagulate by shaking (or boiling), sulphocyanate solution is added immediately, with continual stirring." In a footnote he emphasises, with Volhard, the necessity of considerable training before the eye can discern the "true" end-point of the reaction.

In view of this conflict of statement, and of the value of a rapid method for determining chlorides, it seemed desirable to establish once for all, by systematic experiments, whether Volhard's method is reliable in its original form or requires modification.

The question to be answered was, Is the velocity of the reaction between solid silver chloride and dissolved sulphocyanates really as slow as it is generally supposed to be ? While experience had taught us that it must be appreciable, special preliminary experiments soon indicated that it was astoundingly rapid ; for instance, about a grm. of silver chloride shaken with an equivalent amount of iron sulphocyanate in dilute solution was all but completely transformed into silver sulphocyanate in a very few minutes. To obtain a reasonable percentage of change, and yet a reliable measurement of time, it seemed best to employ equivalent quantities of ammonium sulphocyanate and silver chloride and limit the time of the reaction to two minutes. The apparatus employed consisted of a cylindrical glass vessel with a wide delivery tube appropriately fused on near the bottom. The vessel was blackened on

* Presented before the New York Section of the American Chemical Society, December 7, 1906. From the *Journal of the American Chemical Society*, xxxix., No. 3.

the outside and the delivery tube was closed by a piece of wide rubber hose and a pinch-cock. The silver chloride was kept distributed throughout the volume of the solution by means of a stirrer driven by a gas engine. The temperature of the reacting mixture was about 28°, and it varied by scarcely one-tenth of a degree during the reaction. A good filter of glass-wool and the use of a suction-pump permitted of removing a clear sample of about 50 cc. for analysis in about three seconds. In each experiment, the silver chloride was prepared by precipitating, in a blackened flask, a known volume of standard silver nitrate solution with a slight excess of hydrochloric acid and carefully washing the coagulated precipitate by decantation. The precipitate was washed into the reaction-cylinder, water added to a 180 cc. mark, an equivalent amount of ammonium sulphocyanate solution (20 cc.) thrown in out of a test-tube, and the time noted. At the end of 120 seconds a sample was removed for analysis by opening the rubber hose of the delivery-tube directly over the glass-wool filter.

The analytical method employed was as follows:—An unmeasured volume of solution was precipitated by a known excessive amount of silver nitrate. After filtering, the excess of silver was determined in the solution with standard ammonium sulphocyanate, and an indicator of iron alum; this showed the total amount of silver precipitated. The mixed precipitate of AgCl and AgCNS was then transferred into an Erlenmeyer flask and boiled with an excess of concentrated nitric acid for three-quarters of an hour (Borcher's method). Thereupon water was added, the silver chloride filtered off, and the silver nitrate (from oxidised silver sulphocyanate) determined in the filtrate again by means of standard ammonium sulphocyanate and ferric salt; this showed the amount of silver originally precipitated as sulphocyanate.

Following are the results of three experiments:—

	AgCl.	NH_4CNS.	Volume.	Temperature.	Time.	NH_4CNS changed to NH_4Cl.
	Grm.	Grm.	Cc.		Seconds.	Per cent.
1.	0·286	0·152	200	28·2°	120	45·6
2.	0·286	0·152	200	28·4°	120	43·1
3.	0·286	0·152	200	28·3°	120	41·3
				Average		43

The agreement of the results is more than sufficient for our purpose. But if the astonishing amount of 43 per cent of sulphocyanate is destroyed by only an equivalent amount of silver chloride in two minutes, it must be expected that a large excess of the silver chloride (such as is present during a titration by Volhard's method) would destroy practically all the sulphocyanate in a few seconds. This was, in fact, shown by semi-quantitative experiments; amounts of silver chloride varying between 0·1 and 0·5 grm. were uniformly found to destroy the iron sulphocyanate formed by 2 to 10 drops of a N/15 NH_4CNS solution in from 5 to ten seconds. The following observation is specially convincing: 0·5 grm. of pure silver chloride was placed in 203 cc. of water in a bottle, and 2 cc. of a saturated solution of iron-ammonium alum were added; ½ cc. of a N/15 NH_4CNS solution was then rapidly introduced from a burette, the bottle stoppered, and the whole vigorously shaken for ten seconds. The solution, originally deep-red, was now practically colourless; an "end-point" given by ½ cc. of the reagent had disappeared in ten seconds.

In view of these facts, the following analytical results, obtained by Volhard's method in its original and modified forms respectively, will not appear surprising. First, a set of six determinations were carried out without filtering out the silver chloride (but changing somewhat the rate of stirring). The chloride solution employed was found gravimetrically to contain 2·324 grms. of chlorine per litre. Found by Volhard's method.

	Cl per litre in grms.	Relative error.
1.	2·256	−2·9 per cent
2.	2·277	−2·0 ,,
3.	2·299	−1·2 ,,
4.	2·324	— ,,
5.	2·322	−0·5 ,,
6.	2·276	−2·0 ,,

The same solution precipitated with an excess of silver nitrate and filtered from the silver chloride gave uniformly excellent results:—

	Cl per litre in grms.	Relative error.
1.	2·328	+0·17 per cent
2.	2·328	+0·17 ,,
3.	2·327	+0·13

The conclusion is plain; Volhard's method for the determination of chlorides must be modified by filtering out the silver chloride. While this modification diminishes somewhat the rapidity of the method, it is under all conditions indispensable.

(To be continued).

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, October 24th, 1907.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Messrs. J. V. J. Hayman, J. W. Shepherd, and C. H. Warner were formally admitted Fellows of the Society.

The President reminded Fellows of the loss which the Society had sustained since the previous meeting by the death of Sir William Henry Perkin, Dr. John Clark, Dr. August Dupré, and Mr. F. J. M. Page.

It was announced, also, that on the occasion of the Centenary Celebration of the Geological Society, the following address was presented:—

In the name of the Chemical Society we welcome the present opportunity of offering our warmest congratulations to the President, Council, and Fellows of the Geological Society of London on the occasion of its Centenary Celebration.

It is impossible to overestimate the value of the great work which your Society has accomplished during the past hundred years, both in laying the solid foundations of a new science and in helping to raise on these foundations the stately edifice of Modern Geology.

The connection between Geology and Chemistry has always been, and must ever remain, a very intimate one, and the early history of your Society shows that Chemists a hundred years ago fully recognised that their special branch of Natural Knowledge was destined to play an important part in elucidating those changes in the structure of the earth which fall within the special province of the Geologist.

This association between the two Societies is brought into further prominence by the fact that amongst the thirteen original founders of your Society, we find the names of no less than five celebrated chemists, viz., Arthur Aikin, William Allen, Humphry Davy, W. H. Pepys, and Richard Phillips; whilst within the first few years of your corporate existence the roll of your Fellows includes the names of Thomas Thomson, William T. Brande, Edward Turner, James Hall, W. H. Wollaston, J. F. Daniell, Charles G. Daubeny, and Alexander J. Marcet.

The advances in Modern Petrology, a sub-section of Geology which may be said to have been initiated by your Society, have demanded a still closer union between our respective branches of Science, and in the new ideas introduced within the last decade by the discovery of radio-

activity we see further indications that Physical Chemistry in the near future must influence many of the fundamental doctrines bearing on the age of the earth, and on the various changes which the earth has undergone within the period embraced by Geology.

Signed, on behalf of the Chemical Society,

WILLIAM RAMSAY, President.
ALEXANDER SCOTT, Treasurer.
M. O. FORSTER, } Honorary
ARTHUR W. CROSSLEY } Secretaries.
HORACE T. BROWN, Foreign Secretary.

Certificates were read for the first time in favour of Messrs. John Forbes Bell, Craigmillar, Edinburgh; Edward Joseph Day, M.D., M.R.C.S., L.S.A., Dorchester, Dorset; Frederick Harold Dupré, Mount Edgcumbe, Sutton, Surrey; Percy Vivian Dupré, A.C.G.I., Mount Edgcumbe, Sutton, Surrey; Francis Bridger Dutton, Birch Hall, Windlesham, Surrey; Thomas Rigby Greenough, B.A., Beechwood, Leigh; William Doge Hutchinson, B.A., Lythmore, Tennyson Road, Harpenden; Harry Ingham, M.Sc., 26, Hamilton Street, Bury; Herbert Marsden, B.Sc., Bramford, Ipswich; Herbert Frederick Sankey Marshall, High Street, Burwell; Gerald Hargrave Martin, Delce, Park Road, Wallington; John Edward Langford Moore, Walton Cottage, Loughboro' Park, S.W.; Charles Samuel Mummery, Christ's Hospital, West Horsham; Harold Ramsay Stobie, Clovelly, Craighall Gardens, Edinburgh; Frederick Thomas, B.Sc., 29, Fairhaven Road, St. Annes-on-the-Sea; Harold Munkman Timpany, M.Sc., St. Winifrede's Gardens, Shrewsbury; George Arthur Watson, A.R.C.S.I., 7, Roseneath Villas, Cork; Edward Wheeler, A.C.G.I., 113, Highbury Quadrant, N.; Robert Whymper, A.C.G.I., St. Clare, St. Mary's Road, Ditton Hill; Percy Williams, B.Sc., c/o The Wilhelmina Co., Pontianak, Dutch West Borneo; William John Wilson, A.C.G.I., 28, Windmill Street, Gravesend.

Of the following papers, those marked * were read:—

*192. "*The Constitution of Phenol- and Quinol-phthalein Salts: A Contribution to the Quinonoid Theory of Colour.*" By ARTHUR GEORGE GREEN and PERCY EDGAR KING.

Prof. Green gave an account of the following investigation which has been described in *Ber.*, 1906, xxxix., 2365; 1907, xl., 3724.

Green and A. G. Perkin have adduced evidence as to the constitution of phenol- and quinol-phthalein salts which cannot be reconciled with the indicator theory of Ostwald. On the other hand, the view that the appearance of colour during salt formation is due to a change of type from the lactone or triphenylcarbinol form to the quinonoid form has hitherto not met with general acceptance, largely owing to the failure of repeated attempts to obtain coloured carboxylic esters of these phthaleins.

The authors have now succeeded in preparing the coloured carboxylic esters, not only of the phthaleins themselves, but also of their mono- and di-methyl ethers. These esters, which are orange to red, are extremely unstable, being readily saponified, not only by weak acids or alkalis, but even by water. They form with acids, oxonium salts which are of a deeper colour than the free esters. Whilst the esters of phenolphthalein, $C_6H_4(CO_2Me)\cdot C\begin{matrix}=C_6H_4:O\\ \backslash C_6H_4\cdot OH\end{matrix}$, and of monomethylphenolphthalein, $C_6H_4(CO_2Me)\cdot C\begin{matrix}=C_6H_4:O\\ \backslash C_6H_4\cdot OMe\end{matrix}$, were obtained in the free state, and are more stable than their chlorides, the esters of quinolphthalein and of monomethylquinolphthalein could only be isolated in the form of the oxonium salts, thus, $C_6H_4(CO_2Me)\cdot C\begin{matrix}=C_6H_3(OH)\\ \backslash C_6H_3(OH)\end{matrix}\!\!>O\cdot Cl$.

The esters of dimethylphenolphthalein and of dimethylquinolphthalein (trimethyl derivatives) are only capable of existence as salts, a fact which agrees well with the representation of the chlorides as—

$$C_6H_4(CO_2Me)\cdot C\begin{matrix}=C_6H_4:OMe\\ \backslash C_6H_4\cdot OMe\end{matrix}\!\!<\begin{matrix}H\\ Cl\end{matrix}$$

and—

$$C_6H_4(CO_2Me)\cdot C\begin{matrix}=C_6H_3(OMe)\\ \backslash C_6H_3(OMe)\end{matrix}\!\!>O\cdot Cl.$$

The monomethyl esters of both phthaleins are soluble in alkalis, giving strongly coloured solutions similar to those of the phthaleins themselves, but not decolorised by an excess of alkali. On the other hand, the isomeric lactone ethers are colourless, and do not give coloured salts.

These facts disclose an exact parallelism between the esters and salts of these phthaleins and those of fluorescein and place the quinonoid structure of these substances almost beyond question.

DISCUSSION.

Dr. HEWITT remarked that in certain cases it was very difficult to assign a quinonoid constitution to coloured compounds. He had himself found that the colourless lactone of 2:4:2':4'-tetrahydroxydiphenylacetic acid dissolves in alkalis with a colour extremely like that produced by phenolphthalein, but the colour is discharged on breaking the lactone ring. He had not, however, been able to devise any plausible quinonoid formula for the salts of the lactone.

Prof. GREEN, replying to Mr. Baly, said that the assumption of an oxonium hydrate group in the alkali salts of phenolphthalein was not a necessary deduction from his experiments, but was only advanced in order to give a clearer expression to the analogy in behaviour between these salts and those of quinolphthalein, the latter of which must contain an oxonium group.

Mr. Baly's statement that a quinonoid compound containing oxonium hydrate groupings would be colourless did not rest on any experimental evidence known to him.

The conclusion that the esters described were quinonoid compounds was in no way deduced from their colour, but was a necessary consequence of the experimental facts adduced in the paper, and depended especially on the proof that the methyl group was attached to the carbonyl and the chlorine atom in the ester chlorides to oxygen. These facts, especially in the case of the trimethyl ether of quinolphthalein, scarcely admitted of any other interpretation than that given.

*193. "*Ketene.*" By NORMAN THOMAS MORTIMER WILSMORE.

The gaseous substance produced by the action of a hot platinum wire on acetic anhydride, which was discovered by Dr. A. W. Stewart and the author (*Nature*, 1907, lxxv., 510), has been further examined. As a mean result, it was found that, on exploding one volume of the gas with excess of oxygen, there was a contraction of 1·09 volumes, and that the residual gas contained 1·97 volumes of carbon dioxide, whilst 2·08 volumes of oxygen had disappeared. The corresponding numbers for a gas having the formula C_2H_2O would be 1:1:2:2. A mean value for the density gave a molecular weight of 41·4, instead of 42. The gas has, however, not yet been obtained entirely free from acetylene and higher hydrocarbons. Its marked tendency to condense slowly, on standing, to a brown liquid is one of the chief difficulties in the way of its purification.

The substance combines directly with aniline to form acetanilide, with *o*-toluidine to form aceto-*o*-toluidide, with anhydrous liquid ammonia to form acetamide, and with ethyl and amyl alcohols to form the corresponding acetic esters. It also reacts vigorously with bromine, forming bromoacetyl bromide. As no by-products appear to be formed in these reactions, it may be inferred that the substance is a new anhydride of acetic acid, having the formula $CH_2{:}CO$ or $CH{:}C{\cdot}OH$, and, further, that it is the lowest member of the ketene series. With water, *ketene* gives chiefly acetic acid, but an aldehyde, probably glycollaldehyde, is formed at the same time. Ketene is also produced when an arc is made to burn under the surface of liquid acetic anhydride.

DISCUSSION.

The PRESIDENT suggested that a third possible formula for ketene would be $\begin{matrix} HC \\ \| \\ HC \end{matrix}\!\!>\!O$, a substance having the same relation to acetylene as ethylene oxide has to ethylene. Such a compound might lend itself easily to polymerisation.

194. "*Derivatives of the Multiple Ketene Group.*" By JOHN NORMAN COLLIE.

The group $\cdot CH_2 \cdot CO \cdot$ (which the author proposes to call the "*ketide*" group) can be made to yield by means of the simplest reactions a very large number of interesting compounds, all belonging to classes which are largely represented amongst the compounds obtained from plants.

Illustrations of this were given from the various published papers of the author. It was shown how by uniting more than one of these groups as in ethyl acetoacetate, $H(CH_2 \cdot CO)_2OH$, or in dehydracetic acid, $H \cdot CH_2 \cdot CO)_4OH$, "*polyketides*" are obtained, and from these by means of the simplest reactions, such as hydration, dehydration; oxidation, reduction, loss of carbon dioxide, or action of ammonia, complicated polyketide derivatives result. These are found to represent many of the various types of compounds found in plants.

This can be partly illustrated as follows :—

$H(CH_2 \cdot CO)OH$ Acetic acid. $H[CH_2 \cdot CO)_2OH$ Diacetic acid. $H \cdot CH_2 \cdot CO)_3OH$ Tetra-acetic acid.

$H[CH_2 \cdot CO]_4OH$ Tetra-acetic acid.

With acids, loss of $CO_2 + H_2O$ Dimethylpyrone. — With alkalis, loss of $CO_2 + H_2O$ Orcinol. — With NH_3, loss of $CO_2 + H_2O$ Lutidone.

Hydration Diacetylacetone. → Loss of water

Loss of H_2O from 2 mols. Benzene compound. → With NH_3 *iso*Quinoline compound.

Further loss of H_2O Naphthalene compound.

DISCUSSION.

Dr. M. O. FORSTER inquired what compounds, exactly, were to be classified as polyketides. The name naturally invited comparison with the words polymethylene and polypeptide, the significance of which was perfectly clear, and from that standpoint a polyketide would be a substance built up of the complex, $\cdot CH_2 \cdot CO \cdot x$, with the necessary terminal groups or atoms. The application of the word in Prof. Collie's paper, however, was much more comprehensive, appearing to embrace such heterogeneous types as lactones, pyrone derivatives, benzenoid compounds, and substituted pyridines, and the speaker foresaw considerable danger in launching an entirely novel expression on chemical nomenclature without defining its scope more precisely.

195. "*Production of Orcinol Compounds by the Action of Heat on the Sodium Salt of Ethyl Acetoacetate.*" By JOHN NORMAN COLLIE and EDWIN RODNEY CHRYSTALL.

When ethyl acetoacetate (78 grms.) is mixed with sufficient sodium ethoxide (4·6 grms. of sodium in 50 cc. of ethyl alcohol) to convert about one third of it into the sodium salt and the mixture heated, ethyl acetate, alcohol, and ethyl acetoacetate distil. On treating the viscous residue in the flask with hydrochloric acid, a crystalline compound separates, which is best purified by re-crystallisation from benzene (yield about 7·8 grms.) It has the composition $C_{16}H_{16}O_6$, and melts at 169°. $4C_6H_9O_3 - C_{16}H_{16}O_6 + CH_3 \cdot CO_2Et + 2EtOH + 2H_2O$.

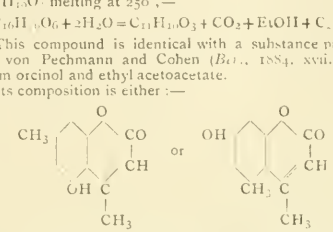
The new compound is soluble in aqueous sodium hydroxide with a deep yellow colour, but the colour changes to pale yellow on warming; acids precipitate from this solution an orange compound of high molecular weight, and alcohol is found in the residue. With sodium hydroxide and chloroform, it gives the orcinol reaction. With bromine, a compound of formula $C_{16}H_{16}O_6Br_2$, melting at 182·5°, is produced.

When warmed with 90 per cent sulphuric acid to about 130—140°, carbon dioxide is evolved, together with alcohol and acetic acid, leaving a compound of formula $C_{11}H_{12}O_3$, melting at 250°,—

$C_{16}H_{16}O_6 + 2H_2O = C_{11}H_{12}O_3 + CO_2 + EtOH + C_2H_4O_2$.

This compound is identical with a substance prepared by von Pechmann and Cohen (*Ber.*, 1884, xvii., 2188) from orcinol and ethyl acetoacetate.

Its composition is either :—



The *monomethyl ether* (m. p. 146°) and the *monoacetyl* derivative were prepared (m. p. 198°).

196. "*A Simple Gas Generator for Analytical Operations.*" By JAMES MCCONNELL SANDERS.

The simple appliance described below has been found to be a convenient and practical substitute for the so-called "constant supply" apparatus of the "Kipp" type. It consists of a glass tube open at one end, and having a fine, almost capillary, tube fused into the other end, as shown in the figure.

The apparatus is charged, for example, for the preparation of hydrogen sulphide by dropping one or two small fragments of ferrous sulphide into the tube so that they lodge in the annular space (A), a few drops of dilute sulphuric acid are then allowed to run into the tube, and the mouth (B) closed with the forefinger. The apparatus may then be introduced into a test-tube or beaker and used as an agitator, the gas escaping by way of the fine interior tube and the orifice (C).

For quantitative work, a larger apparatus is used, and the mouth closed with a cork. For the preparation of a gas which requires the application of a gentle heat, the apparatus is allowed to touch the bottom of the test-tube while immersed in the liquid contents of the latter, and heat is applied to the test-tube itself.

After use, the generation of gas is instantly stopped by directing a stream of water from a wash bottle into the interior, the outside is washed in the same manner, and the apparatus is then ready for use in a subsequent operation. The appliance has been in constant use in the Mexican Customs laboratories for the last five months, and in no case has it been found that the small inner tube showed any tendency to become clogged with precipitate.

(We are indebted to the author for permission to insert the woodcut illustrating this article).

197. "*Some Double Ferrocyanides of Calcium, Potassium, and Ammonium.*" By James Campbell Brown.

The conditions of preparation and the properties of calcium potassium ferrocyanide and calcium ammonium ferrocyanide were explained. These salts have been analysed and their solubilities determined. The calcium potassium ammonium ferrocyanides resulting from the mixture of varying proportions of calcium chloride, potassium ferrocyanide, and ammonium chloride were described, and the conditions for the use of ammonium chloride and potassium ferrocyanide as a qualitative test for calcium were given.

198. "*Determination of Halogen in Organic Substances.*" By James Moir.

The new method described last year by the author (*Proc.*, 1906, xxii., 261) has been improved by adopting the Volhard method of back-titration with standard thiocyanate.

The contents of the crucible after heating are dissolved and treated with a crystal of bisulphite to reduce manganate. A measured quantity of standard silver solution is added, and the mixture is then acidified with nitric acid, heated to 70°, filtered through a Buchner funnel, using hardened paper, and the residue on the filter is extracted with hot dilute nitric acid. The filtrate is then cooled to 40°, and titrated with standard thiocyanate and iron alum.

Each cc. of N/10 silver solution, by difference, = 0·0080 grm. of bromine.

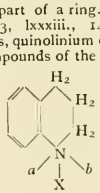
199. "*Racemisation by Alkali as Applied to the Resolution of r-Mandelic Acid into its Optically Active Isomerides.*" By Alex. McKenzie and Hermann August Müller.

It was shown that, as a product of the fractional saponification of *l*-menthyl *r*-mandelate in ethyl-alcoholic solution, either a dextrorotatory or a lævorotatory mandelic acid mixture may be obtained from the same weight of ester, and using the same weight of alkali. The normal action is the formation of a dextrorotatory potassium salt; the formation of a lævorotatory potassium salt under the conditions quoted is abnormal.

Various methods of effecting the changes:—(1) *r*-Mandelic acid ⟹ *r*-mandelic acid and *l*-mandelic acid, and (2) *r*-mandelic acid ⟹ *r*-mandelic acid and *d*-mandelic acid were indicated.

200. "*The Optical Activity of Cyclic Ammonium Compounds.*" By Frank Buckney and Humphrey Owen Jones.

Although it has been shown in a large number of cases that compounds of the type N*abcd*X can give rise to optical activity due to the asymmetric nitrogen atom, yet there is no well-established case of activity when the nitrogen atom forms part of a ring. It was stated previously (*Trans.*, 1903, lxxxiii., 1405) that substituted pyridinium compounds, quinolinium compounds, and tetrahydroquinolinium compounds of the type—



are all devoid of a plane of symmetry, and should be capable of giving rise to optical activity. Several compounds were then examined, but no evidence of activity was obtained.

The following fourteen compounds have now been examined: — 1-Methyl-*a*-picolinium-*d*-camphorsulphonate and *d*-bromocamphorsulphonate, methyl- and benzyl-quinolinium-*d*-camphorsulphonatesmethylkairolinium-1-acetate-*d*-camphorsulphonate and *d*-bromocamphorsulphonate, 1-methyl-1-ethyltetrahydroquinolinium-*d*-camphorsulphonate and *d*-bromocamphorsulphonate, 1-benzyl-1-ethyltetrahydroquinolinium-*d*-camphorsulphonate, benzylkairolinium-*d*-camphorsulphonate, *d*-bromocamphorsulphonate and tartrate, *n*-propylkairolinium-*d*-bromocamphorsulphonate, allylkairolinium-*d*-bromocamphorsulphonate. In the case of the last-mentioned compound only was there conclusive evidence of the existence of optical activity, the *l*-base *d*-acid salt was the less soluble, and had $[M]_D = 198°$, and the *d*-base *d*-acid had $[M]_D = 343°$. The iodide was recovered in small quantity only, but was decidedly active.

201, "*The Action of Phosphorus Pentachloride on Hydroxytrimethylsuccinic Ester.* 1:2-*Dimethylcyclopropane*-1:2-*dicarboxylic Acid* (1:2-*Dimethyltrimethylene*-1:2-*dicarboxylic Acid*)." By Herbert Henstock and Bertha E. Woolley.

The authors have examined the chief chemical and physical properties of 1:2-dimethyl*cyclo*propane-1:2-dicarboxylic acid (1:2-dimethyltrimethylene-1:2-dicarboxylic acid), the optical properties of its diethyl ester having been investigated for them by the late Sir William Perkin. The object of the work was to determine whether this constitution, which was assigned to the acid by Paolini (*Gazzetta*, 1900, [2], xxx., 497), is the correct one, since, if its saturated cyclic character were proved, an important difference is indicated in the behaviour of two so nearly allied substances as bromotrimethylsuccinic anhydride (which yields methylenedimethylsuccinic acid) and chlorotrimethylsuccinic ester when the hydrogen haloid is removed from the molecule. The authors' work confirms that of Paolini.

On the elimination of the hydrogen haloid from chlorotrimethylsuccinic ester, 1:2-dimethyl*cyclo*propane-1:2-dicarboxylic acid is formed.

202. "*The Condensation of Acetaldehyde and its Relation to the Biochemical Synthesis of Fatty Acids.*" By Henry Stanley Raper.

It has been suggested that the formation of fatty acids, in animals, from carbohydrates depends, firstly, on a break-down of the carbohydrate to yield, amongst other products, acetaldehyde, and, secondly, on the condensation of the acetaldehyde leading to the formation of the higher fatty acids. The object of this investigation was to determine whether acetaldehyde on condensation yields the straight-chain compounds which would be necessary for the production of the higher fatty acids, as previous observations on the condensation of aldehydes point to the formation of compounds with branched-chains.

This objection to the above hypothesis has been partly removed, for it has been found that β-hydroxybutyraldehyde, the first product of the condensation of acetaldehyde, on further condensation yields an aldehyde containing eight carbon atoms united in a straight-chain.

203. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part X. *Effect of the Configuration and Degree of Saturation of the Solvent.*" By Thomas Stewart Patterson, Andrew Henderson, and Frank Walter Fairlie.

Solutions of ethyl tartrate in ethyl fumarate, ethyl maleate, and ethyl succinate were examined as regards rotation. Fumaric and maleic esters were found to have much the same effect, which is greater than the effect of succinic ester. The results were discussed from the point of view of combination of solute and solvent.

204. "*Para-toluidine Monohydrate.*" By James Walker and Heather Henderson Beveridge.

p-Toluidine crystallises from water and from aqueous alcohol as a monohydrate which melts at about 41·5°, the melting-point of the anhydrous base being 43·5°. The monohydrate effloresces in the air, but, on the other hand, the anhydrous base absorbs water from air saturated with moisture, and is converted into the monohydrate. In contact with liquid water, the anhydrous base is converted into the monohydrate at all temperatures up to the melting-point of the latter. The pressure of water-vapour over the monohydrate at the ordinary temperature is somewhat more than half that of liquid water.

205. "*Hydrates of some Quaternary Bases.*" By David Cowan Crichton.

Solutions of tetraethylammonium hydroxide, tetrapropylammonium hydroxide, and trimethylsulphine hydroxide were prepared from the corresponding chlorides by means of potassium hydroxide (compare Walker and Johnston, *Trans.*, 1905, lxxxvii., 955).

A *tetrahydrate* and a *hexahydrate* of tetraethylammonium hydroxide were described. When the tetrahydrate is made to lose water at the ordinary temperature, the base decomposes with formation of triethylamine, ethylene, and water.

A *heptahydrate* of tetrapropylammonium hydroxide was separated by cooling the aqueous solution in a freezing mixture. This hydrate melts when raised to the ordinary temperature.

Attempts to prepare a crystalline hydrate of trimethylsulphine hydroxide were unsuccessful.

206. "*Two Volumetric Methods for the Determination of Chromium.*" By Arnold William Gregory and James McCallum.

The authors have modified the persulphate method for the estimation of chromium in iron and steel, with the object of obtaining accurate results in a minimum time.

In the presence of manganese, the permanganic acid, formed simultaneously with the chromic acid, is reduced, either by the addition of a little ammonium chloride or by means of hydrogen peroxide.

The chromic acid formed is titrated with ferrous sulphate solution of known strength.

A method of oxidising the chromium with sodium bismuthate was also described. It is found to give very satisfactory results.

NOTICES OF BOOKS.

India-Rubber and its Manufacture. By Hubert L. Terry, F.I.C. London: Archibald Constable and Co., Ltd. 1907.

In this book we have a pleasantly written account of the properties and uses of india-rubber. Its production is described in detail, and the characteristics of the chief rubbers of commerce are treated in an interesting manner. No attempt is made to go deeply into the chemical nature or properties of rubber, though some allusion is made to the determination of its formula and to the action of certain reagents upon it. The process of vulcanisation is treated from the practical point of view, and the methods of manufacture of mechanical goods are described sufficiently fully to enable the reader to get a grasp of the main outlines of each process, but no attempt is made to go into minute details relating to manufacture, which only the specialist would require and appreciate. The making of tyres is given a chapter to itself, and the gutta-percha and balata industries are also considered. As a very readable contribution to the vast branch of literature which is issued for the benefit of the educated and intelligent general public, who are more concerned with a wide than a deep knowledge, this book has every claim to regard. It is excellently printed and got up, and well provided with illustrations.

Memento du Chimiste. ("Chemist's Memorandum Book.") By A. Haller and Ch. Girard. Paris: H. Dunot et E. Pinat. 1907.

This collection of tables and data relating to pure and applied chemistry is a considerably enlarged edition of the "Agenda du Chimiste," which was issued annually some years ago. The first chapters contains numerical tables of physical constants, thermochemical data, and logarithmic tables, and Chapter II. describes the analysis of simple substances and mixtures for inorganic acids and bases; spectroscopic data are included in this part, and a tabular list shows the most important properties, including the solubilities at different temperatures, of a very large number of inorganic and organic substances. In Chapter III. the analysis of foods and a variety of technical products is treated, and it will thus be seen that the book contains a great deal of information, which is moreover arranged in a very handy form. The smallness of the print would make its constant use very trying, but on the other hand, in spite of the amount of matter it contains, the volume is by no means of an unwieldy size.

A Course of Practical Organic Chemistry. By T. Slater Price, D.Sc., Ph.D., F.I.C., and Douglas F. Twiss, M.Sc., A.I.C. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

The descriptions of methods of preparing organic compounds given in this book are very clear and explicit, and every help is given to the student, who, as one of a large class, is working with but little assistance from a teacher. The book completely covers the syllabus of the Board of Education Examinations, Stages I., II., and III., and also of the B.Sc. degree, and it is divided into three parts, each of which contains the subjects of one stage; although more preparations are described than each student will probably find it practicable to carry out, an excellent experimental course can easily be drawn up by making suitable selections of typical preparations. Methods of testing for various substances and groups of substances are included, and a good systematic scheme of identification should give the student great assistance in this difficult branch of his work. The difficulty of arranging a course of preparations for a beginner, in which he is not obliged to make use of substances of complex structure with which he is not acquainted, in order to prepare the simpler compounds, is to a certain extent met by describing first the purification of ethyl alcohol from methylated spirits or spirits of wine, and then dealing with the preparation of those compounds for which ethyl alcohol can conveniently be used as a starting point. This plan enables the student to do the experiments which require least knowledge and skill first, and at the same time helps him to keep in mind the genetic relations of the substances he is dealing with. The theoretically perfect arrangement has had to be abandoned in some cases, but on the whole the authors have proved very successful in the general plan as well as in the minor details of the book.

CORRESPONDENCE.

ALUMINIUM CARBIDE.

To the Editor of the Chemical News.

Sir,—In the Chemical News for November 15 (vol. xcvi., p. 246) an abstract of a paper on the "Preparation of Aluminium Carbide," by C. Matignon, was given.

We have been working for some time past on the reaction between aluminium and carbon, and have obtained the carbide from wood charcoal, from sugar carbon, and from certain hydrocarbons.

When the carbon and aluminium are present in sufficiently fine powder, the reaction is an exothermic one, and may be started by igniting a portion with a fuse of Mg and BaO_2; but as the reaction proceeds best when carried out in the open air, it is probable that the temperature of the burning Al enables the reaction to proceed, but when the action is once started and the air shut off, the reaction proceeds throughout the mass, which becomes red-hot.

The resulting carbide contains both alumina and aluminium nitride, and gives off H, CH_4, and a very small quantity of a gas smelling of acetylene. This could not have been more than 0·2 per cent of the whole, as this was the diminution with fuming H_2SO_4.

In contact with water the evolution of gas is slow, and in one experiment the evolution of gas has continued for over sixteen days, and is still continuing.

We are preparing aluminium carbide under varying conditions, with a view to discovering whether, at comparatively low temperatures, another carbide can be prepared. —We are, &c.,

HENRY R. ELLIS,
FRANK E. WESTON.

Chemical Laboratory,
The Polytechnic, Regent Street, W.,
November 19, 1907.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 18, October 28, 1907.

Iodomercurates.—A. Duboin.—When ferrous iodide and mercuric iodide are dissolved in water and the mixed liquids allowed to stand in presence of iron, on evaporation crystals of $FeI_2.2HgI_2.6H_2O$ are obtained. If aluminium iodide is substituted for ferrous iodide, the resulting crystals contain oxygen, and have the formula $HgO + 2AlI_3.3HgI_2.15H_2O$. A similar oxyiodide of aluminium and silver can be prepared by dissolving silver iodide in aluminium iodide. Its formula is $2AlI_3.5AgI.2AgO.13H_2O$.

Colloidal Solution of Arsenic.—V. Auger.—The reduction of a hydrochloric acid solution of arsenious anhydride with an aqueous solution of hypophosphorous acid in presence of concentrated alcohol at a temperature below 0° gives a yellow powder, which on drying turns red-brown, and which possesses the property of dissolving immediately in dilute soda, giving a brown colloidal solution. This solution is stable even on boiling, but oxidises rapidly in air, giving arsenite. Alcohol, soda, and potash in excess precipitate brown flakes, soluble in water. Dilute acids, even acetic acid, and all soluble salts precipitate from it brown flakes which are insoluble both in water and in dilute alkalis. When the solution is purified, either by dialysis or by precipitating with alkali and washing with concentrated alkali, a solution is obtained which is free from alcohol, but it has not yet been found possible to free it from traces of phosphorus and of alkali. The author is not at present certain whether the presence of phosphorus is necessary in order that this modification of arsenic may be soluble in alkalis.

Sources of Error in the Determination of Phosphorus in Iron, Cast-iron, and Steel.—G. Chesneau.—In determining the phosphorus in iron by Carnot's method of double precipitation with ammonium molybdate, it is necessary to use a very large excess of the latter reagent, since ammonium phosphomolybdate is soluble in ferric salts, and the following state of equilibrium results:—Am. phosphomolybdate + ferric sulphate $\rightleftharpoons$ ferric phosphomolybdate + am. sulphate, unless a large excess of molybdic acid and ammonium salts is present. In order to avoid loss by washing the ammonium phosphomolybdate, it is best to use, not water containing nitric acid or ammonium nitrate, but pure water. Ammonium nitrate, which in presence of ammonium molybdate renders the precipitation of ammonium phosphomolybdate more complete, dissolves the latter when no ammonium molybdate is present. Acid ammonium molybdate, which is formed when ammonium molybdate is heated for some time above 60°, is soluble in pure water and in water containing nitric acid, but is re-precipitated by ammonium nitrate. Thus if in order to effect complete precipitation the liquid containing phosphoric acid and ammonium molybdate is heated for some time, and thus some acid molybdate is precipitated with the phospho-compound, it is useless to attempt to purify the precipitate by again dissolving in ammonia and acidifying, for the acid molybdate is again partially precipitated by the action of the nitrate produced by the neutralisation of the ammonia. It is therefore best to keep the temperature of the liquid fairly low in order to avoid this error.

MISCELLANEOUS.

National Physical Laboratory.—Mr. Guy Barr, B.A., of Christ's College, Cambridge, has been appointed to an Assistantship in the Metallurgical and Chemical Department of the Laboratory.

Physical Society.—It is announced that the Third Annual Exhibition of Electrical, Optical, and other Physical Apparatus will be held at the Royal College of Science, South Kensington, on Friday evening, December 13th, from 7 to 10 o'clock.

Finsbury Technical College Old Students' Association.—The success which attended the Dinner held in December last has encouraged the council to make arrangements for a similar gathering before the close of the present year. The Second Annual Dinner will take place on Wednesday, December 11, at the Criterion Restaurant, Piccadilly Circus, W., at 7 p.m. for 7.30 o'clock, when the Chair will be taken by Mr. C. G. Redfern, F.C.I.P.A., &c., President of the Association. The cost of the tickets will be five shillings, exclusive of wine. Any Old Students (Day or Evening) should communicate with one of the following:—S. E. GRITTON (Mechanical), Talfourd Cottage, Reigate, Surrey; ERNEST W. MOSS (Electrical), 20, Huddleston Road, Tufnell Park, London, N.; FRANCIS H. CARR (Chemical), "Kelvin," Church Avenue, Sidcup, Kent.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 2nd.—Royal Institution, 5. General Monthly Meeting.
—— Society of Arts, 8. (Cantor Lectures). "Theory of the Microscope," by Conrad Beck, F.R.M.S.
—— Society of Chemical Industry, 8. "Estimation of Naphthalene in Coal-gas and in Spent Oxide of Iron," by C. J. Dickenson-Gair. "Influence of Formol on the Properties of *Funtumia elastica*," by P. Schidrowitz and F. Kaye. "Polarimetric Determination of Sucrose," by F. Watts and H. A. Tempany. "Niam Fat," by J. Lewkowitsch.

WEDNESDAY, 4th.—Society of Arts, 8. "Old Age Pensions," by Sir Edward W. Brabrook, C.B.
—— Society of Public Analysts, 8. "Volumetric Determination of Reducing Sugars" and "Determination of Invert Sugar in presence of Varying Amounts of Cane-sugar," by A. R. Ling and T. Rendle. "Quantitative Separation of Barium from Strontium," by Miss Zelda Kaban. "Action of Dimethyl Sulphate (Valenta's Reagent) upon Oils of the Aromatic and Aliphatic Series" and "Titration with Permanganate in presence of Hydrochloric Acid," by T. W. Harrison and F. M. Perkin. "Routine Methods for the Bacteriological Examination of Water," by A. R. Tankard.

THURSDAY, 5th.—Chemical, 8.30. "Affinity Constants of Bases as Determined by Methyl-orange," by V. H. Veley. "Velocity of Reduction of the Oxides of Lead, Cadmium, and Bismuth by Carbon Monoxide, and the Existence of the Sub-oxides of these Metals," by F. J. Brislee. "Relation between Unsaturation and Optical Activity—Part I., The Menthyl and Borneyl Esters of β-Phenylpropioaic, Cinnamic, and Phenylpropiolic Acids," by T. P. Hilditch. "Constituents of the Essential Oil of Nutmeg," by F. B. Power and A. H. Salway. "Methyl Ethers of some Hydroxy-anthraquinones," by A. G. Perkin. "Colouring-matters of the Stilbene Group—Part IV., The Action of Caustic Alkalis upon Paranitrotoluene and its Derivatives," by A. G. Green, A. H. Davies, and R. S. Horsfall. "Replacement of Alkyl Radicals by Methyl in Substituted Ammonium Compounds," by H. O. Jones and J. R. Hill.

THE CHEMICAL NEWS.

Vol. XCVI., No. 2506.

A NEW ELEMENT, LUTECIUM, OBTAINED BY SPLITTING UP MARIGNAC'S YTTERBIUM.

By G. URBAIN.

In the separations of the elements of the yttrium group, I have always observed that ytterbia gives the most soluble salts. The method which seems to me the best for the preparation of this substance, free from yttria, erbia, and thulia, is the crystallisation of the nitrates (G. Urbain, *Bull. Soc. Ch.*, 1905, xxxiii., 739; *Journal de Chemie Physique*, 1906, iv., 31; "Extract from a Communication to Sir William Crookes," May 5, 1906, *Proc. Royal Soc.*, 1907, lxxviii., 154). In 1905 by this method I obtained 50 grms. of raw ytterbia, answering to Marignac's description (*Comptes Rendus*, lxxxvii., 578).

I propose in this preliminary note to describe shortly the researches which I have been carrying on since then.

In order to determine the atomic weight of ytterbium we are restricted to the analysis of the sulphates of similar products. It seemed to me to be necessary to subject the ytterbia to systematic fractionation in order that I might be sure that its atomic weight and its spectral characteristics were constant.

For this purpose I subjected the nitrates to fresh fractional crystallisations in nitric acid of density 1·3. Thus I obtained, after a very tedious series of fractionations, extending to 22 consecutive fractions, a series of products, the absorption spectra of which I examined first. The first fractions, numbers 9 to 16, showed faintly absorption bands which alone revealed the presence of thulium. I eliminated these fractions. The other fractions which might be considered to be pure ytterbium were transformed into sulphates and analysed.

Far from being constant the atomic weights varied, gradually increasing from 169·9 for fraction 17 to 173·8 for the last fraction, number 31 (see Note). Such a large variation is sufficient to show the complexity of ytterbium.

(Note. — For this first approximation I took O = 16, H = 1, S = 32. These numbers would be increased by about 0·17 if in the calculations I had taken O = 16, H = 1·008, S = 32·06. It may be mentioned that the atomic weight of thulium cannot be 171. It is undoubtedly below 168·5).

I tested the final products of my fractionations for thorium. By the very effective method of Wyrouboff and Verneuil (the action of oxygenated water upon the solution of the neutral nitrates), I succeeded in separating from the earths with the highest atomic weights about a twenty-thousandth of thoria, which could have no influence upon my measurements.

By the arc spectra method I was not able to detect the presence of any impurity in my products thus purified, and there is no doubt that my ytterbia was not a mixture of several constituents.

By photographing on the same plate one above the other the arc spectra of the extreme members of this fractionation, I detected in the spectrum of the last fraction (No. 31) many lines, mostly well marked, which could not be seen in the first fraction (No. 17), or which were very faint in it. Conversely, fraction 17 showed some not very strong lines which were absent in No. 31 and which were probably attributable to thulium. Apart from these lines the two spectra showed a great number of common lines of the same order of intensity. These lines are those which characterise the bulk of the original material, the impurities of which (thulium and the new element) accumulated, the former in the first and the latter in the last of my fractions.

Then I compared the spark spectra of my earths. The differences detected by this method of observation were much clearer than in the case of the arc spectra.

1. The lines in Table I. are the spark spectrum lines, attributable to thulium, which I detected in the fractions of low atomic weight (least soluble nitrates).

Table I.

2869·3	Faint.	3362·7	Fairly strong.
2899·9	Medium.	3425·7	,,
2962·5	,,	3441·6	,,
3050·9	Faint.	3461·9	,,
3131·4	Fairly strong.	3624·5	Faint.
3151·2	Medium.	3712·5	,,
3173·0	,,		

2. The lines in Table II. are the characteristic lines of the new element. They may very easily be detected in the fractions of high atomic weight (most soluble nitrates). They are either found exclusively in these fractions or else are much strengthened in them).

Table II.

*2701·8	Very strong.	3171·5	Fairly strong.
*2754·2	,,	*3183·5	Medium.
*2798·3	,,	3191·9	,,
*2847·6	,,	*3198·2	Strong.
2895·0	,,	*3254·5	Very strong.
*2900·4	,,	3275·5	Fairly strong.
*2911·5	,,	*3312·4	Strong.
*2951·8	,,	*3359·8	,,
*2963·5	,,	*3376·7	,,
2970·0	,,	*3385·6	Fairly strong.
*2989·4	Medium.	*3397·2	Very strong.
3020·7	Very strong.	*3472·6	,,
*3056·8	,,	*3506·8	,,
3058·0	,,	3554·6	,,
*3077·7	,,	3568·0	Strong.
*3080·3	Medium.	3624·1	,,
3118·6	,,	3647·9	,,

The lines marked with an asterisk are the most characteristic of the arc spectrum.

For the limits between which my measurements extend these 34 lines constitute the relatively complete spark spectrum of the new element. (None of these lines are due to scandium, thorium, erbium, thulium, yttrium, or to any common element or rare earth, except the old ytterbium).

I propose lutecium, Lu, derived from the old name of Paris, for the name of this element.

3. The other lines, included between the same limits, and enumerated in the spark spectrum of ytterbium, recently described by Sir W. Crookes, from one of my old preparations (*loc. cit.*), characterise the bulk of the old ytterbium. I propose to give this earth the name neo-ytterbium, Ny, in order to avoid confusion with Marignac's element.

4. The first spectrum of the old ytterbium was described by Lecoq de Boisbaudran (*Comptes Rendus*, 1879, lxxxviii., 1342), to whom Marignac had sent his new earth. It was a band spectrum. When I examined the chlorides of the extreme members of my fractionation by Lecoq de Boisbaudran's method, I noticed that in the earth of low atomic weight (neo-ytterbium) Lecoq de Boisbaudran's γ band was absent. On the other hand, in the earths of high atomic weight, which are very rich in lutecium, this band γ is more marked than the other bands of the spectrum.

The bands α (from $\lambda = 559$ to $\lambda = 552$) and β (from $\lambda = 576$ to $\lambda = 568{\cdot}5$) are thus probably characteristic of neo-ytterbium, and the band γ (from $\lambda = 517{\cdot}5$ to $\lambda = 513$) of lutecium.

To summarise the observations I have described here, Marignac's ytterbium is a mixture of two elements, neo-ytterbium and lutecium. The atomic weight of neo-ytterbium cannot differ much from 170, and the atomic weight of lutecium is not much above 174.

I may mention that Demarçay (*Comptes Rendus*, 1900, cxxxi., 387) denoted by θ an element characterised by lines 4008·2 and 3906·5. He regarded it as distinct from thulium, and included between erbium and ytterbium. I was not able to detect these lines, obtained by the use of a special coil, either in my spark spectra nor in my arc spectra.

Moreover Auer von Welsbach (*Lieb. Ann.*, 1907, cccli., 464) has quite recently announced that by the fractionation of the double oxalate of ammonium and ytterbium he has detected spectral variations which he has not further defined. He did not give any measurements of the lines which he has observed between λ 7000 and λ 5000, and did not specify the elements which he supposes exist in the old ytterbium.—*Comptes Rendus*, 1907, cxlv., 759.

THE MOTHER SUBSTANCE OF RADIUM.

By OTTO HAHN.

As our knowledge of the nature of radio-active phenomena has grown, we have reached the conviction that even radium, which is apparently unchangeable, cannot keep its activity for ever, but that in course of time it must be converted into another inactive product.

Different views are at present held regarding the time which radium takes to undergo this change. The highest value for the decay period—the time in which a given quantity of radium decays to one-half—is 2600 years.

Owing to the great age of the solid crust of the earth, radium would have disappeared long ago, even if the whole earth had consisted of it alone, if we did not suppose that radium itself is continually formed afresh.

This supposition has been fully confirmed. The parent substance of radium is undoubtedly uranium, which undergoes a far slower transformation. It is also certain that one or more intermediate products must exist between uranium and radium, and thus uranium, or rather the so-called uranium X, cannot be the immediate mother substance of radium. A great many investigators have for some time been engaged in the search for this intermediate product.

At the end of 1906 Boltwood (*Phys. Zeit.*, vii., 915) announced that he had succeeded in showing that actinium, which had then been known for some time, was the mother substance. An actinium solution prepared by Boltwood undoubtedly showed an increase in the radium present in it after some months.

Shortly afterwards Rutherford (*Nature*, lxxvi., 126) proved that it was not the actinium itself, but an unknown product occurring with actinium, which produced radium. Giesel, Soddy, Meyer, and v. Schweidler all showed that actinium itself could not be the mother substance.

In a letter to *Nature* (September 26th, 1907) Boltwood described new experiments, confirmed Rutherford's result, and also stated that the hypothetical substance followed the reactions of thorium, and thus must be able to be easily separated, by the aid of these characteristic reactions, from actinium, which resembles lanthanum. In a letter to *Nature* (October 10th), he confirms his supposition, and states that the new substance emits α-rays of a low penetrative power. The product is thus proved to be a new element; Boltwood calls it "ionium."

In reference to this subject I wish to report shortly on experiments which were not quite concluded when Boltwood's statements were published, but which in another perfectly independent way showed that the mother substance of radium follows the chemical reactions of thorium, and can thus be separated with the latter from minerals containing uranium.

In the investigation of a new intermediate product in thorium, which I called mesothorium, I noticed that older "pure" thorium preparations contained relatively large amounts of radium. This was peculiar, for the substance used for the preparation of the thorium, monazite sand, contains only very small amounts of uranium. Naturally only a very small amount of radium corresponds to the small amount of uranium, and this must have been separated from the thorium in the complicated process of preparing pure thorium salts.

Some months ago I therefore began a systematic examination of different old pure thorium preparations to determine the amount of radium they contained. A weighed quantity of pure nitrate was dissolved in pure water, boiled to remove all the radium emanation, and then corked up in a little flask. After a sufficiently long time the contents of the flask were again boiled, the gases were collected in a burette, and some time after, when the thorium emanation had decayed, blown into a suitable electroscope. By comparison with an accurately known quantity of radium under the same conditions in this way the amount of radium present in my thorium nitrate solutions was determined.

I had at my disposal specimens of very different but known age, placed at my disposal by the firm Dr. O. Knöfler, of Berlin. As result I found that the specimens contained more radium the older they were, the oldest specimen of the year 1898 containing the most.

Then I obtained from the firm 100 grms. of quite freshly prepared thorium nitrate. The amount of radium in it was exceedingly small; the whole quantity of 100 grms. of the substance was used to measure it accurately. When referred to equal quantities of thorium the radium present in the new solution was scarcely 1/100 of that in the specimen nine years old.

It could not be assumed that the impurity of the older preparations was the cause of the greater amount of radium present, and it is just as improbable that thorium itself slowly decays to radium. Therefore I assumed that in the technical preparation of thorium another active substance was separated with it. This substance decays to radium, and is thus the long-sought direct mother substance of radium. In order to prove this, at the beginning of August I arranged the following experiments:—

1. One hundred grms. of thorium nitrate, obtained directly from the factory as perfectly fresh, were tested for radium in the way described above, after standing for four days. The result was calculated to the equivalent quantity. It was closed up on August 17th, and again tested on October 10th. The amount of radium was twice as large as before.

2. Forty grms. of thorium nitrate, prepared at the end of April, 1907, were also examined accurately for radium, allowed to stand over the holidays, and tested on October 11th. This amount also showed a considerable increase in the quantity of radium present.

3. Fifty grms. of thorium nitrate, prepared in June, 1907, were precipitated with oxalic acid from acid solution, the radium in the filtrate determined, and again it was allowed to stand over the holidays, and tested in October. In this case there was no increase in the amount of radium. Thus the mother substance is contained in the thorium precipitate. This was accidentally mixed with another preparation, and therefore was not examined further.

4. About 1 mgrm. of radio-thorium (activity about 100,000) was as carefully as possible freed from the small percentage of radium it contained by precipitating it three times with ammonia, and the remaining trace determined on August 15th. The specimen gave the same result on October 14th. The radio-thorium had been prepared from thorianite by precipitating with barium sulphate, and thus could not contain the mother substance of radium, which agrees with the above result.

In order to show the order of magnitude of the amount of radium found in some specimens, I append a few results. The quantity is referred to 100 grms. of thorium nitrate.

One hundred grms. of nitrate which had been obtained a few days before from the factory as only just prepared, contained about 3×10^{-11} grms. of radium bromide. The instruments I had did not allow me to determine the exact amount more accurately.

100 grms. July, 1906, contained $5{\cdot}5 \times 10^{-10}$ grms.
" Feb. 1902, " $2{\cdot}8 \times 10^{-9}$ "
" " 1900, " $4{\cdot}1 \times 10^{-9}$ "

The measurements were carried out with 10 grms. of the substance, except in the case of the perfectly new specimen.

Control experiments with other specimens of thorium are also being arranged.

If the amounts of uranium and thorium present in monazite sand are known, and if it is assumed that the total quantity of thorium and the total quantity of the mother substance of radium are obtained in the thorium preparation, it can be calculated how many grms. of radium are contained in a given amount of thorium nitrate if there is equilibrium between the radium and its parent substance in the thorium.

Now the quantities of uranium and thorium in different specimens of monazite sand, even in those from the same place, vary within certain limits. But it may safely be said that the average amount of uranium in Brazilian monazite sand is 0·3 per cent, and of thorium oxide, roughly, 5 per cent. The amount of thorium is frequently rather higher, but it must not be assumed that the thorium is quite quantitatively extracted in its preparation. Thus, 5 per cent is certainly the right order of magnitude. Now, 1 grm. of uranium in any uranium mineral contains, roughly, $0{\cdot}65 \times 10^{-6}$ grms. of radium bromide. By a simple calculation it may be found from the above assumption that 100 grms. of thorium nitrate + the mother substance of radium in equilibrium with radium must contain, roughly, 2×10^{-6} grms. of radium salt (calculated as bromide).

From this number, and the values obtained above by purely experimental methods for the amount of radium in different specimens of thorium of known age, according to the equation $I/I\infty = 1 - e^{-\lambda t}$, the constant λ can be calculated, and from λ the decay period of radium. Hence, the values found for the decay period from the above results for three different thorium specimens are 3250 years, 2840 years, and 2630 years. As only a mean value is assumed for the amounts of uranium and thorium present, naturally variations in them cause corresponding variations in the decay period. Until more exact measurements are made the values can only be regarded as giving the order of magnitude of the decay period, and can lay no claim to great accuracy. The values found differ widely from a value recently determined by Cameron and Ramsay (*Journ. Chem. Soc.*, xci., 1266) for the decay constant of radium; for these investigators, from the volumes of the emanation developed from radium in a given time, deduced for the mean duration of life of radium 236 years, which gives 163 years for the decay constant. On the other hand, the numbers given above agree satisfactorily with the value 2600 years found by Rutherford. No explanation of the great difference in Rutherford and Ramsay's numbers is as yet forthcoming. Further researches with the newly discovered mother substance of radium will give an explanation of this important question.

Owing to the characteristic properties of "ionium" this new element can easily be completely separated from uranium minerals which contain little or no thorium; with my thorium preparations from monazite sand, which is so poor in uranium, or from monazite itself, it was not possible to get a pure product, as a method of separation from thorium is not yet known.

The part of pitchblende which follows the reactions of thorium will provide the cheapest material for the more thorough investigation of the new substance.

I beg to offer my best thanks to the Jager Foundation, of Berlin, for furnishing me with means for the above research.—*Berichte*, xl., 4415.

A NEW CONSTANT FOR BUTTER ANALYSIS.

By T. R. HODGSON, B.A., A.I.C.

The analysis of butter is a constant source of trouble to the public analyst, partly because the present constants are variable for different samples and partly because the constants of the most common adulterants approach so closely to those of butter that it is possible to add to a very good sample of butter comparatively large quantities of the adulterant before the constants are brought down to the lowest value which is consistent with pure butter.

Another circumstance which makes the carrying out of the law with regard to pure butter almost an impossibility is that the adulteration is now carried on scientifically, and the unscrupulous man is able to add large quantities of other fats and oils to a good sample and smaller quantities to inferior samples, knowing full well that the resulting mixture will pass all the tests at the command of the analyst.

The author hopes that the constant described in this paper may go some way towards a mitigation of this evil.

The constant depends upon the oxidation with potassium permanganate of the acids obtained from butter fat after saponification with caustic potash and acidification with sulphuric acid. The author has found that the quantity of oxygen required to oxidise a given quantity of the saponified fat is, in the case of butter fat, invariable.

The method used is as follows:—The sample of butter is melted in a water-oven, and filtered through a dry filter-paper; 1 grm. of the filtered fat is then weighed out into a flask, and 25 cc. of a half normal alcoholic solution of caustic potash are added; the flask is then attached to a reflux condenser, and the whole is heated on a boiling water-bath for thirty minutes.

After the saponification the flask is detached from the condenser, and the solution is evaporated to dryness on a boiling water-bath; 50 cc. of distilled water are then added to the residue, and the whole again evaporated to dryness; this operation being continued until the whole of the alcohol is driven off. After the whole of the alcohol has been driven off, the residue is dissolved in water, and made up to 1000 cc.; 20 cc. of this solution are measured out into a beaker, and 50 cc. of a tenth-normal solution of potassium permanganate added and 50 cc. of a roughly 50 per cent solution of sulphuric acid; the beaker is then placed on a boiling water-bath for half-an-hour, and the excess of potassium permanganate is titrated back with a tenth-normal solution of oxalic acid, or with a standard solution of ferrous ammonium sulphate, preferably the latter.

Twenty-one samples of butter were examined, nineteen of which were of known purity, and were obtained in and around Birmingham, and two contained a proportion of margarine.

Sample.	$K_2Mn_2O_8$ used. Cc.	Sample.	$K_2Mn_2O_8$ used. Cc.
A.	41·8	M.	41·8
B.	41·8	N.	41·8
C.	41·8	O.	41·8
D.	41·8	P.	41·8
E.	41·8	Q.	41·8
F.	41·9	R.	41·8
G.	41·8	S.	41·8
H.	41·9	T.	30·0
I.	41·9	X.	36·2
K.	41·8	Z.	41·8
L.	41·8		

The Samples T and X were more or less mixed with margarine. As will be seen from the above figures the number of cc. of the permanganate solution used remains practically constant throughout.

From the number of cc. of permanganate solution used, the number of grms. of oxygen absorbed in the oxidation

of 1 grm. of the butter fat can be calculated, and this number multiplied by 100 gives what, for want of a better name, I propose to call the "oxygen equivalent."

This number, in the case of pure butter fat, is practically invariable, and is 167·2.

An attempt was first made to obtain the constant by direct titration with the permanganate solution, but the only result was a copious black precipitate of oxide of manganese and no apparent end-point.

The influence of time on the oxidation is not very marked; the oxidation was carried out as before, with the exception that the time of heating on the water-bath varied from five minutes to one hour; the variation in the number of cc. of permanganate solution used was 37·2 at the end of five minutes to 41·8 at the end of one hour; with consequent variation in the "oxygen equivalent" from 148·8 to 167·2; at the end of thirty minutes the oxidation ceases, and, apparently, no oxidation occurs between that time and one hour.

Time. Minutes.	$K_2Mo_2O_8$ used. Cc.	Oxygen equivalent.
5	37·2	148·8
10	37·6	150·4
15	37·9	151·6
20	38·2	152·8
25	40·0	160·0
30	41·8	167·2
35	41·8	167·2
40	41·8	167·2
45	41·8	167·2
50	41·8	167·2
55	41·8	167·2
60	41·8	167·2

It was the intention of the author in undertaking this piece of work to devise a method by which it would be possible to detect the presence of cocoanut oil in butter, and he hopes that the results given in this and two following papers may at least lead to such a method.

Analytical Department,
University of Birmingham.

A NECESSARY MODIFICATION OF VOLHARD'S METHOD FOR THE DETERMINATION OF CHLORIDES.*

By M. A. ROSANOFF and ARTHUR. E. HILL.

(Concluded from p. 265).

2. *On the Determination of Bromides and Iodides.*

We now turn to the determination of bromides. A solution made up of 200 cc. of water, 2 cc. of a saturated solution of iron-alum, and 1 drop of a solution of NH_4CNS, was thrown upon 0·5 grm. silver bromide in a stoppered bottle, and the mass vigorously shaken. After ten seconds no change of colour was noticeable; after thirty seconds the colour had become but slightly less intense. It seemed probable, therefore, that in ordinary titrimetric work the end-point would not be affected by the presence of solid bromide. This is, in fact, shown by the following four results, of which Nos. 1 and 2 were obtained by titration in presence of the bromide, Nos. 3 and 4 with the bromide filtered out.

1. .. .. 5·366 grms. Br per litre
2. .. .. 5·366 ,,
3. .. .. 5·357 ,,
4. .. .. 5·359 ,,

The slight disparity of the results obviously lies within the limits of experimental error.

With reference to the determination of iodides, we have been unable to observe any diminution in the intensity of iron sulphocyanate coloration even after the coloured solution had been shaken with silver iodide for one-half hour.

It is thus clear that in the determination of bromides and iodides it is unnecessary to filter out the silver precipitate before titrating with sulphocyanate.

3. *The End-point.*

The reactions between dissolved sulphocyanates and solid silver halides are, like all similar reactions, reversible. For instance, $AgCl + CNS^- \rightleftarrows AgCNS + Cl^-$. The transformation of sulphocyanates by silver chloride has been discussed above. The opposite reaction may be readily demonstrated by shaking silver sulphocyanate with an ammonium chloride solution containing some iron-ammonium alum: dissolved sulphocyanate shows up in a very short time.

In equilibrium,—

$$C^+_{Ag} \cdot C^-_{Cl} = S^2_{AgCl} \text{ and } C^+_{Ag} \cdot C^-_{CNS} = S^2_{AgCNS};$$

where C stands for concentration and S for solubility in pure water (both in molecules per litre). By division,—

$$\frac{C^-_{Cl}}{C^-_{CNS}} = \frac{S^2_{AgCl}}{S^2_{AgCNS}}.$$

Taking Böttger's recently solubility figures (*Zeit. Phys. Chem*, 1903, xlvi., 602), $S_{AgCl} = 1{\cdot}06 \cdot 10^{-5}$ and $S_{AgCNS} = 8{\cdot}27 \cdot 10^{-7}$. Hence,—

$$\frac{C^-_{Cl}}{C^-_{CNS}} = \frac{1{\cdot}12 \cdot 10^{-10}}{6{\cdot}84 \cdot 10^{-12}} = \text{about } 164.$$

Since similar salts are dissociated to the same degree, the ratio of the total (dissociated and undissociated) amounts of chloride and sulphocyanate in equilibrium with AgCl and AgCNS is also about 164. (The general theory of such equilibria in salt solutions was first given by Nernst in his "Theoretische Chemie," Ed. 1, Stuttgart, 1893, p. 426; Ed. 3, Stuttgart, 1900, p. 498). When, therefore, the ammonium sulphocyanate contained in a drop of solution is brought into contact with silver chloride, 164/165 of it are transformed into chloride and only 1/165 remains sulphocyanate. In other words, to produce the permanent colour-effect that a single drop of NH_4CNS would have in the absence of AgCl, no less than 165 drops of NH_4CNS are required when AgCl is present. Such intensity of colour is, however, unnecessary. We find that the eye can detect the coloration due to about 1/15 of a drop of N/10 NH_4CNS in 200 cc. of water containing 5 cc. saturated iron-alum solution. To establish such a coloration permanently in the presence of AgCl, $165 \div 15 = 11$ drops of sulphocyanate solution are required. If the amount of silver nitrate required to precipitate the chloride in a given solution is about 25 cc., the error committed in a perfect sulphocyanate titration in the presence of the silver chloride would amount to about 2 per cent. Ordinarily it will be smaller; the smaller the less diligently one stirs the solution.

It might be similarly shown that in the case of bromides and iodides the interference of the precipitates with the end-point is negligible (see Note). Dynamic theory is thus throughout in agreement with the verdict of our experiments.

Note.—Taking Böttger's figures (*loc. cit.*) for the solubilities of AgBr and AgCNS and Kohlrausch and Dolezalek's figure (*Ber. Berlin Akad.*, 1901, p. 101) for

* Presented before the New York Section of the American Chemical Society, December 7, 1906. From the *Journal of the American Chemical Society* xxxix., No. 3.

the solubility of AgI, the ratios of the solubility products involved are as follows :—

$$\frac{S^2_{AgBr}}{S^2_{AgCNS}} = \frac{C^-_{Br}}{C^-_{CNS}} = \frac{2{\cdot}03 \cdot 10^{-13}}{6{\cdot}84 \cdot 10^{-13}} = \text{about } 0{\cdot}3$$

(that is, of a drop of sulphocyanate added, three-thirteenths will be changed to bromide, but ten-thirteenths will remain unchanged) ;

$$\frac{S^2_{AgI}}{S^2_{AgCNS}} = \frac{C^-_{I}}{C^-_{CNS}} = \frac{2{\cdot}25 \cdot 10^{-16}}{6{\cdot}84 \cdot 10^{-13}} = \text{about } 0{\cdot}00033$$

(that is, of a drop of sulphocyanate added, only about 1 3000 will be changed to iodide).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1907.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Messrs. P. C. Austin, C. Hollins, and L. G. Killby were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward de Barry Barnett, 40, Queensborough Terrace, Hyde Park, W. ; Frederic William Caton, B.A., B.Sc., 6, King Street, Snow Hill, E.C. ; George Hugh Crisp, B.A., 62, Gainsboro' Road, Crewe ; Claude Scott Fawcitt, Darlington, England ; and Shimoga S.M.Ry., India.

Of the following papers, those marked * were read :—

*207. "*Gaseous Nitrogen Trioxide.*" By Herbert Brereton Baker and Muriel Baker.

The authors have found that liquid nitrogen trioxide can be converted into the gaseous state if it is dried completely. Seventeen determinations of the density of the gas have been made by Victor Meyer's method in very dry nitrogen. Several different preparations were used and the densities varied from 38 to 62. The density corresponding to the formula N_2O_3 is 38, and it is concluded that there is partial polymerisation to the double molecule N_4O_6. The analysis of the substance gave 63·12 per cent of oxygen (mean of five experiments), the calculated value for the trioxide being 63·09. Determinations of the molecular weight by the cryoscopic method in dried benzene gave 83 and 83·2 for one sample and 95 for another. The liquid is green at the ordinary temperature, but becomes blue below $-2°$. It does not solidify at $-80°$, but in liquid air it solidifies to a mass of very dark blue crystals.

Discussion.

Dr. Veley asked if the authors had examined the effect of sunlight on nitrogen trioxide, as it appeared possible that the variations in composition and density of the several samples examined might be due to this cause.

The observation of the authors that nitrogen trioxide does not dissolve in water to form nitrous acid, as such, seemed of especial interest ; although this acid was frequently represented as a reagent in chemical change, yet those who had worked on the subject had begun to realise that nitrous acid was possibly no better than a convenient fiction.

Dr. Divers called attention to the fact that, two years ago, Raschig (*Zeit. Angew. Chem.*, 1905, xviii., 1281), and Rây and Gañguli (*Proc.*, 1905, xxi., 280) showed, independently, that nitric oxide distinctly forms nitrogen trioxide with oxygen before it goes on to produce nitric peroxide, and thus furnished chemical evidence, for the first time, of the existence of nitrous anhydride, N_2O_3, in the gaseous state.

Dr. Baker, in reply, stated that sunlight had not been observed to exert any effect on nitrogen trioxide.

*208. "*The Atomic Weight of Tellurium.*" By Herbert Brereton Baker and Alexander Hutcheon Bennett.

The investigation of tellurium and the possibility of its containing another element has been the subject of study for the last thirteen years. The following methods were used in attempting to split up the element :—(1) Fractional crystallisation of telluric acid prepared by two distinct processes. (2) Solution of barium tellurate in water. (3) Fractional distillation of (*a*) tellurium, (*b*) tellurium tetrachloride, and (*c*) tellurium dioxide. (4) Conversion of tellurium into the hydride. (5) Fractional electrolysis of tellurium tetrachloride and tetrabromide. (6) Fractional precipitation of tellurium tetrachloride by water.

In none of these processes was any difference found in the various fractions. Two methods were described for finding the equivalent of the element. The first, which depends on the reduction of the dioxide to the element by means of sulphur, gave 127·60 as the atomic weight (mean of twenty-five determinations), and the second, depending on the conversion of the element into the tetrabromide, gave 127·61 (mean of eighteen determinations).

Discussion.

The President remarked that no research is final, but this one must go a long way to settle the question of the homogeneity of tellurium.

Dr. Percy Williams, many years ago, carried out at University College some experiments on the subject. Tellurium, purified by crystallisation of its double bromide with potassium, gave, on reducing its oxide with hydrogen and absorbing volatilised metal with silver foil, the number 127·6 for the atomic weight. The double bromide, owing to the crystals retaining mother-liquor, was not adapted for an atomic weight determination.

*209. "*The Isomerism of the Double Sulphites of Sodium and Potassium.*" By Michael Harry Godby.

By neutralising potassium hydrogen sulphite with sodium hydroxide and sodium hydrogen sulphite with potassium hydroxide, two solutions are produced from which opaque, greasy crystals are obtained with some difficulty. They are of somewhat variable composition as regards water of crystallisation, and contain the metals in unequal atomic proportions, generally about 60 atoms of sodium to 40 of potassium.

These crystals, when heated with ethyl iodide to 130—140° in a sealed tube, yield a salt which can be crystallised from boiling alcohol and contains ethyl, sodium, potassium, iodine, and SO_3. In each case, there are present about 76 atoms of potassium for every 24 of sodium.

An attempt was made to prepare the double sulphites from the two solutions by precipitating with alcohol, as recommended by Röhrig. Fine powdery, white crystals were obtained having almost exactly the composition required for $KNaSO_3$.

These crystals, when heated with ethyl iodide as before and the product extracted with boiling alcohol, gave a white, finely-crystalline salt, which was re-crystallised from boiling alcohol. This salt, whether obtained from the solution made originally by neutralising potassium hydrogen sulphite with sodium hydroxide or by neutralising sodium hydrogen sulphite with potassium hydroxide, contained sodium, potassium, ethyl, SO_3, and iodine in the same proportions, and approximated fairly closely to the salt prepared by Schwicker (*Ber.*, 1889, xxii., 1728) to which he ascribes the formula $4(KEtSO_3)NaI$, but contained 28 atoms of sodium to 72 of potassium, instead of 20 to 80 respectively.

There is no evidence for the existence of two isomeric salts, $KO{\cdot}SO_2Na$ and $NaO{\cdot}SO_2K$.

*210. "*Studies in the Camphane Series.* Part XXIV. *Camphoryldithiocarbamic Acid and Camphorylthiocarbimide.*" By MARTIN ONSLOW FORSTER and THOMAS JACKSON.

Camphoryldithiocarbamic acid, C_8H_{14} , prepared from aminocamphor and carbon disulphide, is much more stable than compounds of this class which have been hitherto described, and does not decompose below its melting point, 128°. The *methyl* ester, $C_{12}H_{19}ONS_2$, melts at 147°, and is resolved into camphorylthiocarbimide and methyl mercaptan at 170°; the *benzoyl* derivative, $C_{18}H_{21}O_2NS_2$, crystallises from petroleum in colourless, silky needles melting at 105°. Nitrous acid oxidises the dithiocarbamic acid to the thiocarbimide and sulphur, but if amyl nitrite is added to an ethereal solution of the acid an intermediate *compound*, $C_{11}H_{15}ONS_2$, is produced, which melts at 110°, and breaks up readily into sulphur and the mustard oil.

Camphorylthiocarbimide, C_8H_{14} , obtainable in a variety of ways from the dithiocarbamic acid, melts at 106·5°, and combines readily with bases, but less freely with alcohols; *camphorylthiocarbamide*, $C_{11}H_{18}ON_2S$, arising from it by the action of dry ammonia, melts at 180°, and *dicamphorylthiocarbamide*, $C_{21}H_{32}O_2N_2S$, obtained by prolonged treatment with water, melts at 176°. *Camphorylphenylthiosemicarbazide*, $C_{17}H_{23}ON_3S$, occurs in two modifications, melting at 183° and 163° respectively; these are distinguishable by a variety of colour reactions, and by the readiness with which the less fusible form passes into the *anhydride*, $C_{17}H_{21}N_3S$, which melts at 235°.

DISCUSSION.

MR. W. C. REYNOLDS observed that supersaturated solutions of the alkaloid hyoscyamine in some solvents, such as water and wet ether, behaved in a similar manner to the case described by Dr. Forster.

MR. A. C. CHAPMAN remarked that the glucoside apiin was another substance in which a remarkable relationship existed between the jelly and the crystalline forms.

The PRESIDENT suggested the analogy between the phenomena mentioned by Dr. Forster and other gentlemen and superfusion. Alcohol, when cooled, solidifies to a glass; on standing for a couple of days, crystallisation sets in, as indeed it does in the long run with ordinary glass. In the instances adduced by Dr. Forster, no doubt surface tension phenomena are concerned.

*211. "*The Vapour Pressures of Triethylamine, of 2 : 4 : 6-Trimethylpyridine, and of their Mixtures with Water.*" By ROBERT TABOR LATTEY.

A study of the total pressure curves for these mixtures shows that they conform to the type predicted by theory. The partial pressure curves can be calculated by a form of the Duhem-Margules equation. In both cases the curves show a maximum where the compositions of vapour and liquid are identical. At temperatures where the miscibilities of the components are limited there are indications of a second maximum inside the "unreal" parts of the curves.

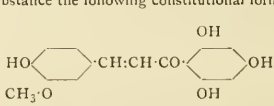
*212. "*Liquid Triethylamine.*" By ROBERT TABOR LATTEY.

A comparison of the vapour pressures and critical constants of triethylamine and other liquids leads to the belief that the amine is a unimolecular liquid. This is confirmed by a determination of the temperature-coefficient of the molecular surface energy.

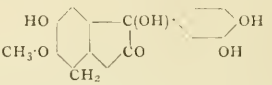
*213. "*Note on the Constitution of Homoeriodictyol.*" By FREDERICK BELDING POWER and FRANK TUTIN.

At the meeting of the American Pharmaceutical Association held in September, 1906, a paper was communicated by the authors entitled "Chemical Examination of Eriodictyon" (*Proc. Amer. Pharm. Assoc.*, 1906, liv., 352; Abstr., 1906, ii., 885). In this communication, we described the isolation and properties of three new crystalline substances, one of which possessed the formula $C_{16}H_{14}O_6$, and was designated homoeriodictyol. Early in the following year, G. Mossler (*Annalen*, 1907, cccli., 233) described the results of an examination of the same drug. Mossler had also isolated from *Eriodictyon* leaves the substance possessing the formula $C_{16}H_{14}O_6$, but proposed to name it "eriodictyonon."

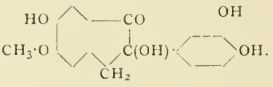
At the time of the appearance of the latter paper, we were engaged in further work on homoeriodictyol, the results of which (*Trans.*, 1907, cxi., 889) led us to assign to this substance the following constitutional formula—



We have recently been favoured by Dr. Mossler with a reprint of a paper communicated by him to the Academy of Sciences in Vienna (*Sitzungsber. K. Akad. Wiss. Wien.*, June, 1907, [2], cxvi.) at a time when he was unaware of our second investigation. In this most recent paper he sets forth the conclusion that homoeriodictyol ("eriodictyonon") is represented by one of the following formulæ :—



or—



It is stated by Mossler that the action of alkalis on homoeriodictyol results only in the formation of a red resin, but this is not the case, as it was shown in our second communication that the product of this action although highly coloured and containing a considerable amount of tarry matter, consists to a large extent of a mixture of phloroglucinol and ferulic acid. It follows from this that neither of the above formulæ proposed by Mossler can correctly represent the constitution of homoeriodictyol, as substances possessing such configurations could not possibly give rise to phloroglucinol. On the other hand, a ready explanation of the formation of all the substances obtained from homoeriodictyol by Mossler is afforded by assigning to this compound the constitution which we have proposed.

Although the observation, recorded by Mossler, that the action of bromine on homoeriodictyol is one of substitution, and not of addition, might be taken as evidence in support of the conclusion that the latter substance was saturated, it cannot be considered as proof that an ethylenic linking is not present.

The statement made by Mossler that homoeriodictyol possesses optical activity, is in direct conflict with our views regarding the constitution of this substance, as the formula we have proposed contains no asymmetric carbon atom. We had previously examined tetra-acetylhomoeriodictyol polarimetrically, but without being able to detect any optical activity, and have now repeated this experiment with the same result. Homoeriodictyol, also, has now been examined in this direction, and we can definitely state that our material is optically inactive. So far as we are aware, therefore, no facts have yet been recorded which are not in harmony with the formula we have assigned to homoeriodictyol.

214. "*The Alkyl Compounds of Gold. Diethylauric Bromide.*" (Preliminary Note). By William Jackson Pope and Charles Stanley Gibson.

Auric bromide reacts vigorously with magnesium ethyl bromide in ethereal solution, and from the product *diethylauric bromide*, $(C_2H_5)_2AuBr$, has been separated; this is the first alkyl gold compound to be described.

Diethylauric bromide dissolves in the ordinary organic solvents, but is insoluble in water. It crystallises in long colourless needles which melt at 58° with slight decomposition; on rapid heating, it decomposes explosively at about 70°. The compound has an odour resembling that of bromocamphor, and volatilises on warming in a vacuum. It is much more readily acted on by reagents than is the recently discovered trimethylplatinic iodide, $(CH_3)_3PtI$; thus the former yields crystalline products on treatment with ammonia and nitric acid, whilst the latter is unaffected by those reagents.

The study of the alkyl compounds of the metals of Groups I. and VIII. of the periodic classification is being continued.

215. "*The Interaction of Methylene Chloride and the Sodium Derivative of Ethyl Malonate.*" (A Correction). By Frank Tutin.

In a paper bearing the above title (*Trans.*, 1907, xci., 1141), three crystalline substances were described as by-products of the reaction which takes place when methylene chloride is heated with the sodium derivative of ethyl malonate. It has now been ascertained that one of these substances, described as "the yellow sodium salt," is the sodium derivative of "ethyl dicarboxyglutaconate," and had been formed from chloroform which was present as an impurity in the methylene chloride. The acid obtained by the hydrolysis of this sodium compound, and to which the formula $C_{10}H_{12}O_8$ was assigned, must therefore have been glutaconic acid, $C_5H_6O_4$.

216. "*Preparation of Aliphatic Nitro-compounds by the Interaction of the Alkyl Iodides and Mercurous Nitrite.*" By Prafulla Chandra Ray and Panchanan Neogi.

By the interaction of mercurous nitrite and the alkyl iodides, namely, methyl, ethyl, *iso*propyl, and *iso*amyl iodides, the corresponding nitro-compounds and the esters are formed. In this respect, mercurous nitrite behaves exactly like silver nitrite. The yields obtained were as follows:—[(*a*) = with silver nitrite, (*b*) = with mercurous nitrite]. Methyl iodide (28 grms.) gave (*a*) methyl nitrite, 3·6 grms., and nitromethane, 4·0 grms., (*b*) 2·1 grms. and 2·6 grms. respectively. Ethyl iodide (60 grms.) gave (*a*) ethyl nitrite, 12·8 grms., and nitroethane, 12·1 grms., (*b*) 8·8 grms. and 9·2 grms. respectively. *iso*Propyl iodide (34 grms.) gave (*a*) *iso*propyl nitrite, 8·0 grms., and nitro-*iso*propane, 6·3 grms., (*b*) 4·1 grms. and 3·8 grms. respectively.

*iso*Amyl iodide (76 grms.) gave (*a*) *iso*amyl nitrite, 3·2 grms., and nitro*iso*pentane, 12·4 grms., (*b*) 3·2 grms. and 7·8 grms. respectively.

217. "*Some Mercury Derivatives of Camphor.*" By James Ernest Marsh and Robert de Jersey Fleming Struthers.

When camphor is heated with an alkaline solution of mercuric iodide, mercury derivatives of camphor are formed. By treatment with glacial acetic acid, *camphor dimercuri-iodide*, $C_{10}H_{14}O,Hg_2I_2$, is precipitated. The filtrate, when diluted with water, gives with potassium iodide, or, better, with a solution of mercuric iodide in potassium iodide, an orange precipitate of the double salt, $C_{10}H_{15}O,HgI + HgI_2$. This, on treatment with potassium iodide in neutral solution, gives *camphor mercuri-iodide*, $C_{10}H_{15}O,HgI$, which is pale yellow. The above-mentioned acetic acid solution also gives with potassium chloride and bromide white precipitates of *camphor mercuri-chloride*, $C_{10}H_{15}O,HgCl$, and *camphor mercuri-bromide*, $C_{10}H_{15}O,HgBr$, respectively, which, however, have not yet been obtained quite free from iodide.

218. "*Contributions to the Chemistry of the Terpenes. Part II. The Oxidation of Limonene with Chromyl Chloride.*" By George Gerald Henderson.

When a dilute solution of chromyl chloride in carbon disulphide is slowly added to a similar solution of limonene, an *additive product*, $C_{10}H_{16},2CrO_2Cl_2$, is precipitated. This compound is a brown powder, which begins to decompose in moist air, and at once reacts with water, yielding a solution of chromic chloride, some resinous matter, and a brown viscous liquid insoluble in water. When subjected to distillation in steam, the brown liquid yields a further quantity of resinous matter and a clear yellow oil, which is composed of an aldehyde, a ketone, and a very unstable substance containing chlorine as well as oxygen. The *aldehyde*, $C_{10}H_{14}O$, is a strongly odorous oily liquid, b. p. 221—222° 755 mm. It yields a crystalline *semicarbazone*, m. p. 156°. It is unsaturated, and on exposure to air it is converted into the corresponding *acid*, $C_{10}H_{14}O_2$, which forms small colourless crystals, m. p. 172°. The *silver* salt of the acid crystallises in small white prisms. Boiling dilute nitric acid converts the aldehyde slowly into *p*-toluic acid; this is also the chief product when the aldehyde is oxidised with a dilute solution of potassium permanganate. The *ketone*, $C_9H_{12}O$, is the chief constituent of the oxidation product. It is an almost colourless oily liquid with a strong odour, b. p. 112—113 15 mm. It is unsaturated. The *semicarbazone* of the ketone crystallises with one molecule of methyl alcohol in colourless prisms which quickly effloresce in the air. After heating at 100°, it melts at 205°. When heated with ammonium formate in a sealed tube, the ketone is converted into the formyl derivative of an amine, from which the free *amine*, $C_9H_{13}\cdot NH_2$, is obtained by hydrolysis with alcoholic potash. It is a colourless oily liquid with a disagreeable odour and an alkaline reaction, and is almost insoluble in water. The hydrochloride and the sulphate of the amine are deliquescent, and very readily soluble in water or alcohol; the *platinichloride*, which is very sparingly soluble in water, crystallises in small brownish yellow needles. The chlorinated oxidation product is so unstable that it could not be isolated.

219. "*The Synthesis of Acridines and Phenonaphthacridines. Tetra- and Hexa-methylacridines, Dimethylphenonaphthacridines, Dixylylmethylenediamines.*" By Alfred Senier and Arthur Compton.

By the interaction of methylene dichloride and xylidines, with or without xylenols, two methylenediamines are formed which by means of Ullman's method of substitution (*Ber.*, 1903, xxxvi., 1019) gave rise to two corresponding acridines. One of the latter can also be obtained by heating the methylenediamine to a higher temperature, whereas the other cannot. This is explained by assuming that, when the *p*-position with respect to the amino-group in the arylamine is not substituted, the methylenediamine first formed is changed by metastasis to a methylene-benzidine (*pp*-diaminodiarylmethane) from which no acridine can result.

When, however, the *p*-position is occupied by an alkyl group, the metastatic action produces an *oo*-diaminodiaryl-methane from which an acridine is easily derived. By the interaction of methylene dichloride and mixtures of xylidines and naphthols, corresponding dimethylphenonaphthacridines are obtained.

The following compounds were described:—*Di*-1 : 3 : 4-*xylylmethylenediamine* (compare Senier and Goodwin, *Trans.*, 1902, lxxxi., 284). 1 : 3 : 7 : 9-*Tetramethylacridine*; its *platinichloride*, *aurichloride*, and *picrate*. *Di*-1 : 4 : 5-*xylylmethylenediamine* and its *platinichloride*. 1 : 4 : 6 : 9-*Tetramethylacridine* and its *aurichloride*. 1 : 3 : 4 : 6 : 7 : 9-*Hexamethylacridine* (compare Senier and Goodwin, *loc. cit.*). N-α

Di-ψ-*cumylmethylenediamine*. 9 : 11-*Dimethylpheno*-| -CH3

naphthacridine and its *platinichloride*. 9 : 11-*Dimethyl*-

N-β
pheno- | *-naphthacridine* (compare Ullmann, *Chem.*
CHα

N-α
Centr., 1901, ii., 568). 8 : 11-*Dimethylpheno-* | *-naphth-*
CHβ
acridine and its *platinichloride*. 8 : 11-*Dimethylpheno-*
N-β
| *-naphthacridine* and its *platinichloride*.
CHα

220. "*Chemical Examination of the Root and Leaves of Morinda longiflora.*" By Marmaduke Barrowcliff and Frank Tutin.

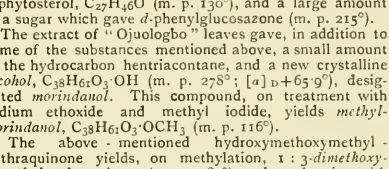
The root and leaves of *Morinda longiflora*, G. Don, a West African plant known as "Ojuologbo," and stated to possess valuable medicinal properties (*Journ. Soc. Arts*, 1905, liii., 1069), have been chemically examined.

The ground materials were extracted with hot alcohol, and the resulting extracts separately investigated. No alkaloid was present in either material.

The extract yielded by the root gave a small quantity of a *hydroxymethoxymethylanthraquinone*, $C_{16}H_{12}O_4$ (m. p. 290°), and a small amount of a monoethylether of alizarin. It also yielded, in addition to resins and other amorphous products, formic, acetic, butyric, palmitic, and citric acids, a phytosterol, $C_{27}H_{46}O$ (m. p. 130°), and a large amount of a sugar which gave *d*-phenylglucosazone (m. p. 215°).

The extract of "Ojuologbo" leaves gave, in addition to some of the substances mentioned above, a small amount of the hydrocarbon hentriacontane, and a new crystalline *alcohol*, $C_{38}H_{61}O_3{\cdot}OH$ (m. p. 278°; $[\alpha]_D$ +65·9°), designated *morindanol*. This compound, on treatment with sodium ethoxide and methyl iodide, yields *methylmorindanol*, $C_{38}H_{61}O_3{\cdot}OCH_3$ (m. p. 116°).

The above-mentioned hydroxymethoxymethyl-anthraquinone yields, on methylation, 1 : 3-*dimethoxy-2-methylanthraquinone* (m. p. 181°), and, on heating with 70 per cent sulphuric acid, it gives 1 : 3-dihydroxy-2-methylanthraquinone. It must therefore be represented by one of the following formulæ :—



On heating with hydriodic acid, it yields a *dihydroxymethylanthranol*, $C_{15}H_{12}O_3$ (m. p. 235°).

The monomethyl ether of alizarin is identical with the compound of this nature which was isolated by Perkin and Hummel (*Trans.*, 1893, lxiii., 1174) from "Chay root."

Neither of the extracts possessed any pronounced physiological activity.

221. "*Ethyl α-cyano-γ-phenylacetoacetate.*" By Arthur Richard Smith and Jocelyn Field Thorpe.

Contrary to the observation of Haller, it is found that ethyl *α*-cyano-*γ*-phenylacetoacetate, $CH_2Ph{\cdot}CO{\cdot}CH(CN)CO_2Et$, is a well-defined, crystalline substance, which melts at 25°, and distils without decomposition at 178° (20 mm.). The compound is a strong acid, readily decomposing carbonates, and yielding salts which can be recrystallised from water without undergoing dissociation. The alkali salts are not acted on by alkyl iodides, but if the silver salt is treated, in dry ether solution with ethyl iodide a mixture of *ethyl α-cyano-γ-phenyl-α-ethylacetoacetate*, $CH_2Ph{\cdot}CO{\cdot}CEt(CN)CO_2Et$, and *ethyl α-cyano-β-ethoxy-γ-phenylcrotonate*, $CH_2Ph{\cdot}C(OEt){:}C(CN)CO_2Et$, is produced. The former is a liquid boiling at 190—191° (20 mm.), and the latter a solid melting at 66°. Characteristic derivatives of ethyl α-cyano-γ-phenylacetoacetate and of the two forms of its ethyl derivative were described.

222. "*Aromatic Amides and Imides of Camphoric Acid.*" By William Ord Wootton.

The substance obtained by the action of nitrous acid on camphorylphenylhydrazide is found to be *N-nitroso-camphorylphenylhydrazide*, $C_8H_{14}{<}\begin{matrix}CO\\CO\end{matrix}{>}N{\cdot}N(NO){\cdot}C_6H_5$, m. p. 157°, and not a nitro-compound as stated by E. M. Chaplin (*Ber.*, 1892, xxv., 2565). *N-Nitrocamphoryl-phenylhydrazide*, $C_8H_{14}{<}\begin{matrix}CO\\CO\end{matrix}{>}N{\cdot}N(NO_2){\cdot}C_6H_5$, may be prepared by the action of nitric acid and acetic anhydride on camphorylphenylhydrazide, and forms colourless prisms melting and decomposing at 115—116°.

Camphoryl-4-bromophenylhydrazide,—

$$C_8H_{14}{<}\begin{matrix}CO\\CO\end{matrix}{>}N{\cdot}NH{\cdot}C_6H_4Br,$$

and *camphoryldibromophenylhydrazide* have been prepared, together with their *N-nitroso-* and *N-nitro-*derivatives. It is found in each case that the nitroso-derivatives are pale yellow, whilst the nitro-compounds are colourless. The fact that the latter are readily reduced with elimination of ammonia indicates that the nitro-group is not attached to the benzene nucleus.

Camphoric anhydride combines with *p*-bromoaniline at 120° to form *4-bromophenyl-α-camphoramic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}CO{\cdot}NH{\cdot}C_6H_4Br$, m. p. 207°. Reduction of the *nitro*-derivative of this acid yields *4-bromo-3-aminophenyl-α-camphoramic acid*, m. p. 207.° *4-Bromo-3-aminophenylcamphorimide*, $C_8H_{14}{<}\begin{matrix}CO\\CO\end{matrix}{>}N{\cdot}C_6H_3Br{\cdot}NH_2$, has also been obtained. These two amino-compounds are optically active, and it is the author's intention to utilise them and certain of their derivatives in the study of racemic aldehydes.

Camphoric anhydride and aminoazobenzene combine to form *4-benzeneazophenyl-α-camphoramic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_5$, m. p. 223—224°. On reduction, *4-aminophenyl-α-camphoramic acid* is obtained.

223. "*The Melting-point of* d-*phenylglucosazone.*" By Frank Tutin.

During the past few years a number of plants have been submitted to exhaustive investigation in the Wellcome Chemical Research Laboratories, and in all cases where sugar was found to be present the osazones were prepared. In a number of instances the phenylosazone obtained melted at a temperature considerably higher than that at which *d*-phenylglucosazone is stated to fuse, namely 205.° Several of these preparations melted at or above 215°, whilst the osazone yielded by the sugar contained in the leaves of *Gymnema silvestre* (Power and Tutin, *Pharm. Journ.*, 1904, lxxiii., 234) fused at 218—219°. Analyses of these preparations of high melting-point showed that they were the osazones of hexoses, and as the only compound of this class stated to melt above 206° is *a*-acrosazone (m. p. 217°), it was at first thought that they must be identical with this compound and were derived from inactive sugars.

It was, therefore, deemed of importance to recrystallise and examine a number of the specimens of osazones which had been prepared from plant sugars by different workers in these laboratories. With this end in view experiments were instituted with the object of finding a better means of purifying osazones than by re-crystallisation from alcohol, and it was ascertained that the use of pyridine was attended with excellent results. The osazone was dissolved in a small quantity of boiling pyridine, hot alcohol and subsequently a little water added, when, on allowing the mixture to cool, the osazone separated in a pure condition.

Specimens of osazones prepared from plant sugars were then recrystallised in this manner, with the results shown in the accompanying tables.

Source of sugar.	Original melting-point of osazone.	Melting-point after re-crystallisation.
Brucea antidysenterica (fruit) ..	205°	217°
,, ,, (leaves) .	205	215—216
Gymnema sylvestre (leaves) ..	218—219	217
Aethusa cynapium (herb)	218	217
Grindelia camporum (herb) ..	205—206	216
Chailletia toxicaria (fruit)	211—212	216
Eriodictyon Californicum (leaves)	205	216—217
Morinda longiflora (root)	215	216
Lippia scaberrima (herb)	210	216—217
Ipomoea purga (tuber)	217—218	217—218
Olea Europaea (bark)	216	217
Micromeria Chamissonis (herb) .	205	217

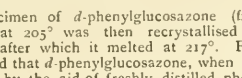
A specimen of *d*-phenylglucosazone (from dextrose) melting at 205° was then recrystallised in a similar manner, after which it melted at 217°. Furthermore, it was found that *d*-phenylglucosazone, when prepared from dextrose by the aid of freshly distilled phenylhydrazine, and avoiding a too protracted period of heating, exhibited an initial melting-point of 216°.

It is evident, therefore, that *d*-phenylglucosazone, when pure, melts at about 217°, and not at 205° as stated by Fischer (*Ber.*, 1884, xvii., 579).

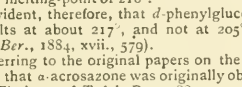
On referring to the original papers on the subject it will be found that α-acrosazone was originally obtained melting at 205° (Fischer and Tafel, *Ber.*, 1887, xx., 1093), and that it was only after careful purification that it exhibited a melting-point of 217° (*Ibid.*, p. 3389). It is evidently owing to the fact that *d*-phenylglucosazone was not submitted to an equally elaborate process of purification (*loc. cit.*) that the correct melting-point of this substance was not initially observed.

224. "*The Interaction of Cyanodihydrocarvone, Amyl Nitrite, and Sodium Ethoxide.* Part II. *The Constitution of the Products.*" By Arthur Lapworth and Elkan Wechsler.

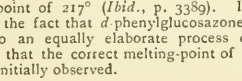
The compound obtained as the product in the above reaction and referred to in the first paper (*Trans.*, 1907, xci., 978) as "the lactam" (L), has the constitution—



The derived amino-acid (A), when acted on by acids, is converted into the "lactonic base" (B),—

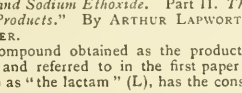


and the "lactonic acid,"—



successively.

On reduction with ferrous hydroxide in alkaline solution, the latter yields pure *d*-homoterpenoyl methyl ketone,—



ammonia, and carbonate.

The isomeric "lactonic base" (B'), erroneously assigned $[\alpha]_D$ 6·21, is quite inactive, and on reduction yields inactive homoterpenoyl methyl ketone. This base is therefore a racemic form of B. The isomeric lactam (L') is strongly active, but also yields the inactive keto-lactone on reduction.

PHYSICAL SOCIETY.

Ordinary Meeting, November 22nd, 1907.

Prof. J. Perry, F.R.S., President, in the Chair.

Mr. S. Skinner exhibited specimens of Singing Sand from New England.

The specimens shown were from two sea-beaches in New England, one at Manchester, Mass., and the other near Small Point, Maine. The beaches are alike in character in being surrounded by hard rock walls and in not having streams which might bring silt flowing through them. The sands are consequently very clean and free from small particles; and this especially so after each tidal washing. The sand consists chiefly of angular clear quartz fragments. Mr. Skinner has been able to verify most of the facts observed by Mr. Carus Wilson (*Nature*, 1891), viz.:—1. The sounds are best obtained by plunging a hard plunger into a glazed cup containing the sand. 2. After a time the production of the sounds becomes difficult. 3. The sounding may be restored by washing, which presumably removes fine powder formed by attrition between the particles. 4. It is necessary that the displacement of the sand by the plunger should occur easily. If there is resistance due to the shape of the vessel, or due to clogging by dust, the sounding is stopped. The theory put forward in "Sound" by Professors Poynting and Thomson seems a reasonable explanation. They consider that Osborne Reynolds's discovery that there is an arrangement of minimum volume of a number of equal spheres in contact may afford a key to the phenomenon. "We may suppose the sand to consist of equal spheres, arranged when undisturbed so as to occupy minimum volume. When disturbed the mass may pass through many successive minima of volume before coming to rest."

Mr. L. Bairstow exhibited a Micromanometer

The instrument exhibited was one of two which are in regular use at the National Physical Laboratory for measurements of pressures due to air currents. It was designed by Prof. Chattock and Mr. Fry for Dr. Stanton's work on "Air Pressures on Plane Surfaces," and is described in the *Proc. Inst. C. E.*, clvi., Part 2. An earlier description of a somewhat similar tilting gauge was also given by Prof. Chattock in 1901 (*Phil. Mag.*, Jan., 1901). When the pressures on the two sides of the gauge are balanced the whole of the liquids employed are in their zero positions, and errors due to capillarity and viscosity are avoided. The gauge exhibited has a sensitiveness of 1/10,000 of an inch of water and a range of three-quarters of an inch of water. The gauge is slightly sensitive to temperature due to the expansion of the castor-oil used, but the changes are small and easily allowed for by taking time-readings of the zero. The gauge is not suitable for rapidly varying pressures, as considerable distortions of the oil-surface leads to an irregularly displaced zero.

Mr. A. Campbell drew attention to the question of capillarity, and asked if the working of the instrument was affected by changes in the surface-tension and angle of contact of the liquids in the gauge.

Prof. H. A. Wilson suggested the use of liquids without appreciable vapour pressure.

Mr. Bairstow, in reply, thought that the effects of surface-tension would not interfere with the correct working of the instrument.

A Diabolo Experiment was shown by Mr. C. V. Boys.

Mr. Boys exhibited a diabolo spool which has the peculiar merit that no one can spin it. It is based upon the following principle:—Either the ordinary spool of commerce, which has its moment of inertia about its axis of rotational symmetry a minimum, or a spool not generally made which has the corresponding moment of inertia a maximum, has stable rotation about this axis or about a transverse axis, *i.e.*, if it is temporarily rotating about an axis inclined to one or other, it will tend to shift its

momentary axis of rotation, and gradually settle down so as to spin about one or other. If, however, the spool is so proportioned that the moment of inertia is identical about any axis, it has no tendency to spin stably about any particular axis, and the axis of rotation wanders about so rapidly that it cannot be spun. A heavy conical sheet projecting equally on either side of the vertex, whose semivertical angle is equal to $\tan^{-1}\sqrt{2}$, has this property; but such an ideal construction is impracticable. All added matter beyond the sheet in the direction of the axis makes the momental ellipsoid more prolate, while any outside the sheet makes it more oblate. Treating then the ideal cone as a skeleton and clothing it with matter within and without, a material double hollow cone may be made of the form of a diabolo spool but with the dynamical properties of a sphere. It is preferable, however, to make the spool with an axial hole and with a slight preponderance of moment of inertia about its rotational axis. It will then spin perfectly. It may, however, be easily adjusted by the insertion of a stick which is cut off of such a length as to make the moments of inertia equal, as tested by suspension from a torsion wire. It is remarkable how close must be the adjustment before spinning becomes impossible. If the difference in periods of oscillation is as much as 1 in 35, spinning is quite easy; the periods should not differ more than 1 per cent. If the stick which makes the adjustment perfect when centrally placed is pushed out a little to one side, the adjustment is disturbed and spinning becomes easy, but now being unbalanced the spool, under the tilting couple of gravity and the string, precesses, and precesses faster as the rate of spinning is slower, so that if such a stick is made to project considerably on one side, it requires some dexterity to follow it through 180° or so before the proper spin is acquired, when the slower precession is easily followed. Mr. Boys considered the diabolo spool a useful addition to the apparatus of a classroom.

Prof. H. A. Wilson exhibited a Gyroscope illustrating Brennan's Monorailway.

A gyroscope is mounted in bearings so that it can spin about a horizontal axis and precess freely. The gyroscope is further mounted at the top of a rectangular framework. The axis of spin of the wheel is first placed at right angles to the plane of the framework. Attached to the vertical axis about which the precessional motion occurs is a short crank with a spiral spring attached, so that when precession occurs in any direction the precessional couple is increased and the top returns towards its initial position. The oscillations of the gyroscope about its mean position become continually larger until the stability of the arrangement disappears.

The Chairman remarked that the subject of gyroscopic action was an important one because gyroscopes would probably be used a great deal in the future. Although engineers knew all about translational motion, few were acquainted with rotational motion. The analogies between centrifugal force and the action of a gyroscope were very close. Prof. Perry then went into the case of steadying a rolling ship, and showed how the differential equations obtained could be modified to admit of easy solution.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Miss Joyce Burton Buckley, Dr. L. Gottschalk, Mrs. Robert Home, Dr. D. G. Johnstone, Sir Edwin Ray Lankester, K.C.B., Mr. S. F. G. Osborne, and Miss E. A. Stoney, M.A., were elected Members. Prof. L. J. Troost (Paris), Prof. Albin Haller (Paris), and Prof. Walther Victor Spring (Liege), were elected Honorary Members. The Special Thanks of the Members were returned to Lord Sanderson for his Donation of Five Guineas to the Fund for the Promotion of Experimental Research at Low Temperatures.

NOTICES OF BOOKS.

Inorganic Chemistry. By E. I. Lewis, B.A. (Cantab.), B.Sc. (Lond.). Cambridge: The University Press. 1907.

In this book the author endeavours to follow the strictly logical method of teaching chemistry, and to build up the science by studying each substance from the point of view of its composition first, using for all reactions only those compounds which have previously been thus studied. Thus the first chapter deals with the composition of water; then, hydrogen and oxygen being regarded as known, they are supposed to be supplied to the student as he requires them from a gas-holder, and the elements of the air are studied. Then common salt is electrolysed, and thus the learner gets acquainted with sodium and chlorine, and so on. A more philosophical aspect of chemistry is put before the student than is usual in elementary text-books, and on the whole fuller and more detailed information is given, which marks the book out as likely to be very useful for revision, and also to help the teacher to prepare his lessons. The discussion of the atomic theory is clear, and abstention from the use of formulæ and symbols until the theory is thoroughly understood is undoubtedly a wise procedure. Whether the logical method as expounded in the book is so far superior to all others as the author thinks, probably teachers will find they have reason to doubt. The electrolysis of water involves complex apparatus, and the help of an agent of which the beginner is quite ignorant, and from this point of view seems hardly suitable as an elementary study. However, in many ways the book is really valuable, and probably the students who use it will find it very helpful for preparation for an examination, for which it is often found that the modern text-book of elementary chemistry is quite useless.

Die Elektrochemische und Elektrometallurgische Industrie Grossbritanniens. ("The Electro-chemical and Electro-metallurgical Industries of Great Britain"). By John B. C. Kershaw. Translated into German by Dr. Max Huth. Halle-a.-S.: Wilhelm Knapp. 1907.

In this book a clear account is given of the present state of the electrochemical and electrometallurgical industries of Great Britain. The author has generally ascertained his facts from personal visits to the factories and works he describes, although he has to chronicle the exhibition of a decided disinclination on the part of many firms to provide him with information relating to plant, processes, and output. In spite of this difficulty he has succeeded in producing what must be regarded as the most complete short summary of the subject which has yet been published. The historical development of each branch is fully and interestingly treated, and where official data were for any reason unobtainable, estimates or information from other sources have been supplied. A tabular statement giving statistics as to the growth and relative importance of the different branches of the electrochemical industry would probably be found useful. An appendix to the book contains a literal translation into German of eleven of the most important English patents, beginning with Watts' method of decomposing salts and other substances, granted in the year 1851, and giving the specifications of patents taken out since that date relating to improvements in processes or apparatus.

Chlormethyl Sulphate.—J. Houben and H. R. Arnold. —Chlormethyl sulphate, $SO_4{<}^{CH_2.Cl}_{CH_3}$, may be prepared by passing vapours of sulphur trioxide over cooled monochlor methyl ether: $SO_3 + Cl.CH_2.O.CH_3 = CH_3.SO_4.CH_2.Cl$. The product of the reaction is a yellow or dark coloured heavy oily liquid. It can be purified by distillation *in vacuo*, and it is then found that the pure substance is a liquid of specific gravity 1·473 at 18°. It is fairly stable in air, and slowly decomposes with water, giving methyl sulphuric acid, formaldehyde, and hydrochloric acid.—*Ber.*, xl., No. 15.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 19, November 4, 1907.

Disecondary Butylene Monochlorhydrine. — K. Krassousky.—Five years ago the author described a method of preparing $H_3C{-}CH{-}CH{-}CH_3$ (OH, Cl), which did not differ essentially from the process recently described by Louis Henry. This method was based upon the action of hypochlorous acid upon butylene, obtained either by allowing zinc ethyl to act on acetic aldehyde and then transforming the secondary alcohol thus prepared into iodide and decomposing with alcoholic potash, or else by adding zinc to butylene bromide in alcoholic solution.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 14, 1907.

Oxidation of Hydrazine.—A. W. Browne and F. F. Shetterly.—When hydrazine sulphate and ammonium metavanadate react in presence of sulphuric acid a secondary reaction takes place, which leads to the formation of hydrazoic acid and ammonia; the importance of this reaction depends upon the experimental conditions, such as the proportions of the substances, the temperature, the rate at which the metavanadate is added to the solution of hydrazine sulphate, and the amount of sulphuric acid present. The highest yield of hydrazoic acid yet obtained is 13·55 per cent of the theoretical yield according to the equation $2N_2H_4 + 2O = N_3H + NH_3 + 2H_2O$. The highest yield of ammonia is 21·3 per cent of the theory. The method of determining hydrazine by means of ammonium metavanadate proposed by Hofmann and Küspert is theoretically affected by a percentage error, which is numerically equivalent to the yield of hydrazoic acid, if the nitrometer method is used, but is much smaller with the oxygen method. The error with Lunge's nitrometer is about 4·5 per cent, and with the oxygen method about 1 per cent.

Reduction of Arsenic Tri- and Pentasulphides to Disulphide.—R. Ehrenfeld.—When a hydrochloric acid solution of stannous chloride acts upon arsenic tri- or pentasulphide they may be reduced to the disulphide according to the following equations:—

$$As_2S_3 + SnCl_2 + 2HCl = As_2S_2 + SnCl_4 + H_2S$$
$$As_2S_5 + 3SnCl_2 + 6HCl = As_2S_2 + 3SnCl_4 + 3H_2S.$$

This reaction explains the formation of a red precipitate when arsenic is detected in presence of tin. The reduction cannot be effected by the agency of other chlorides, such as arsenic trichloride, antimony trichloride, phosphorus trichloride, ferrous chloride, or chromous chloride. When carbon disulphide is heated in closed tubes with a hydrochloric acid solution of stannous chloride, most of the disulphide is unaltered after exposure to a temperature of 100° for twelve hours, although a small proportion of it undergoes the following reaction: $CS_2 + 2H_2O = CO_2 + 2H_2S$, and on opening the tube there is a distinct smell of sulphuretted hydrogen.

Dihydroxy - diaquo - diammino - chromic Salts, $\left[\begin{matrix}HO\\HO\end{matrix}Cr\begin{matrix}(OH_2)_2\\(NH_3)_2\end{matrix}\right]X$.—A. Werner and J. Dubsky.—By the action of bromine upon an aqueous solution of Reinecke's salt, $\left[Cr\begin{matrix}(SCN)_4\\(NH_3)_2\end{matrix}\right]K$, a green salt, dibromo-diaquo diammino-chromic bromide, $\left[Br_2Cr\begin{matrix}(OH_2)_2\\(NH_3)_2\end{matrix}\right]Br$, is obtained. When pyridine is added to a solution of this salt in water a crystalline precipitate of a monohydrate of dihydroxy - diaquo - diammino - chromic bromide, $\left[(HO)_2Cr\begin{matrix}(OH_2)_2\\(NH_3)_2\end{matrix}\right]Br + H_2O$, is formed. The extra molecule of water can be removed by drying at 60°. Other salts of the same constitution, which the authors have prepared, are the iodide and sulphocyanide, neither of which contains the additional molecule of water. The dithionate has the composition $\left[(HO)_2Cr\begin{matrix}(OH_2)_2\\(NH_3)_2\end{matrix}\right]_2S_2O_6 + H_2O$. No sulphate of this dihydroxy series could be prepared, although attempts to obtain it giving hydroxy-triaquo-diammino-chromic sulphate, $\left[(H_3N)_2Cr\begin{matrix}OH\\(OH_2)_3\end{matrix}\right]SO_4 + H_2O$. In acetic acid solution the following condition of equilibrium is established:—

$$\left[\begin{matrix}(H_2O)_2\\(H_3N)_2\end{matrix}Cr(OH_2)_2\right](O.CO.CH_3)_2 \rightleftarrows \left[\begin{matrix}(H_2O)_2\\(H_3N)_2\end{matrix}Cr(OH)_2\right]Br + 2HO.CO.CH_3.$$

The power of the hydroxyl of dihydroxy-diaquo-diammino-chromic bromide to bind acetic acid is so small that even in presence of a fairly large excess of the acid some of the unchanged hydroxy salt is still present, *i.e.*, a part of the tetraquo salt is hydrolysed to dihydroxy salt. No dihydroxy salt is precipitated when potassium bromide is added to a solution of the dihydroxy salt in a mineral acid; *e.g.*, hydrobromic acid.

Dihydroxy-tetrammino-platinum Compounds. — A. Werner.—The investigation of the dihydroxy-tetrammino-platinum compounds shows that phenomena which seem to point to isomerism are really to be ascribed to the existence of stable dimorphic forms. Thus, the sulphate, $[(HO)_2Pt(NH_3)_4]SO_4$, when prepared by one method, crystallises partly in the anhydrous form, and partly with 4 molecules of water; by another method the anhydrous form is always obtained. It is impossible to convert the anhydrous into the hydrated form by re-crystallisation, but by introducing crystals of the hydrated form into solutions of the anhydrous modification the transformation is readily effected. The electrolytic dissociation of the salt occurs as follows:— $\left[\begin{matrix}HO\\HO\end{matrix}Pt(NH_3)_4\right]X_2 \rightarrow \left[\begin{matrix}HO\\HO\end{matrix}Pt(NH_3)_4\right]^{++} + 2X^-$.

Hydroxy - pentammino - cobaltic Salts. — A. Werner. — These salts are formed by the action of ammonia upon aquo - pentammino - cobaltic salts, $\left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]X_3 + NH_3 = \left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]X_2 + NH_4X$. They have a basic reaction in aqueous solution. With ammonium salts the reverse action takes place:— $\left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]X_2 + NH_4X = \left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]X_3 + NH_3$. The author has prepared the iodide, chloride, bromide, nitrate, and dithionate of this series, and has found that they all contain one or more molecules of water, with the exception of the first. The salts do not behave like basic salts of the aquo-pentammino series, but their properties and reactions all show that they are hydroxy-pentammino salts. By the addition of hydrochloric acid the following reaction is produced: $\left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]Cl_2 + HCl = \left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]Cl_3$. The product when heated gives up water as follows:— $\left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]Cl_3 = H_2O + \left[Co\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right]Cl_2$, and the chloro - pentammino - chloride by the action of concentrated ammonia is converted into hexammino-chloride, $\left[Co\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right]Cl + NH_3 = [CO(NH_3)6]Cl_3$. When the actions of the aqueous solutions of the chlorides of the four series upon litmus are compared the following results are obtained:—

$\left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]Cl_2$	$\left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]Cl_3$	$\left[Co\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right]Cl_2$	$[Co(NH_3)_6]Cl_3$
Basic.	Acid.	Neutral.	Neutral.

MISCELLANEOUS.

Physical Society Exhibition.—At the Exhibition to be held by the Physical Society on Friday evening, December 13th (from 7 p.m. to 10 p.m.) at the Royal College of Science, South Kensington, the following firms will be exhibiting:—Messrs. R. and J. Beck, Ltd.; Cambridge Scientific Instrument Co., Ltd.; Casella and Co.; A. C. Cossor; Crompton and Co.; Elliott Bros.; Everett, Edgcumbe, and Co.; Evershed and Vignoles, Ltd.; Clark Fisher and Wadsworth; Gambrell Bros.; J. J. Griffin and Sons; A. Hilger, Ltd.; Leslie Miller; Nalder Bros. and Co.; Nalder Bros. and Thompson, Ltd.; Newton and Co.; R. W. Paul; James Pitkin and Co.; Ross, Ltd.; Alexander Wright and Co.; and also the Meteorological Office. From the Programme, of which we have received an advance proof, there appear to be many items of considerable interest to both Physicists and Electrical Engineers. We understand that invitations have been given to the Institution of Electrical Engineers, the Faraday Society, the Optical Society, and the Röntgen Society. Admission, however, except to Fellows of the Physical Society, will be by ticket only, and therefore Members of the Societies just mentioned desiring to attend the Exhibition should apply to the Secretaries of the Society to which they belong.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution before Easter:—Sir David Gill, a Christmas course of six illustrated lectures on "Astronomy, Old and New," adapted to a juvenile auditory; Dr. A. A. Gray, two lectures on "The Internal Ear of Different Animals"; Prof. F. J. Haverfield, two lectures on "Roman Britain—(*a*) Its Frontiers and Garrison, (*b*) Its Interior Civilisation"; Prof. W. Stirling, six lectures on "Membranes, their Structure, Uses, and Products"; Dr. E. A. Wallis Budge, three lectures on "The Egyptian Sudan, its History, Monuments, and Peoples, Past and Present"; Prof. W. W. Watts, two lectures on "(i.) The Building of Britain, (ii.) Recent Light on Ancient Physiographies"; Major Martin Hume, three lectures on "The Story of the Spanish Armada"; Prof. W. Somerville, two lectures on "Wood, its Botanical and Technical Aspects"; Prof. Sir John Rhys, two lectures on "Celtic": Mr. R. T. Glazebrook, two lectures on "Physics"; Mr. R. Lydekker, two lectures on "(i.) The Animals of Africa, (ii.) The Animals of South America"; Prof. Gisbert Kapp, "The Electrification of Railways"; Mr. Lionel Cust, two lectures on "Anthony Van Dyck"; Mr. Selwyn Brinton, three lectures on the "Art of Florence"; and Prof. J. J. Thomson, six lectures on "Electric Discharges through Gases." The Friday Evening Meetings will commence on January 17, when Prof. T. E. Thorpe will deliver a Discourse on "The Centenary of Davy's Discovery of the Metals of the Alkalis." Succeeding Discourses will probably be given by Colonel David Bruce, Prof. E. Rutherford, Mr. Humphry Ward, Dr. C. W. Saleeby, Sir Oliver Lodge, Prof. W. A. Bone, Prof. J. Milne, Prof. A. E. H. Love, The Hon. R. J. Strutt, Lord Montague of Beaulieu, Prof. J. J. Thomson, and other gentlemen.

MEETINGS FOR THE WEEK.

Monday, 9th.—Society of Arts, 8. (Cantor Lectures). "Theory of the Microscope," by Conrad Beck, F.R.M.S.

Wednesday, 11th.—Society of Arts, 8. (Aldred Lecture). "Radioactive Phenomena," by Sir William Ramsay, K.C.B., &c.

Thursday, 12th.—Society of Arts, 4.30. "Big Game in India," by R. Gilbert, F.Z.S.

Friday, 13th.—Society of Arts, 8. (Shaw Lecture). "Industrial Poisons—Lead and Phosphorus, with Special Reference to the Manufacture of Lucifer Matches," by Prof. Thomas Oliver, M.D.

—— Physical, 7. Exhibition of Electrical, Optical, and other Physical Apparatus, in the Physics Laboratory, Royal College of Science, Imperial Institute Road, South Kensington.

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2507.

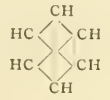
THE ORIGIN OF COLOUR IN ORGANIC COMPOUNDS.

By PERCY MAY.

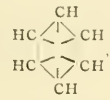
Part I.

The study of the cause of colour in organic compounds is of necessity a modern one. The vast majority of coloured compounds are of the "aromatic series," and before the time of Kekulé we had practically no knowledge of the constitution of these bodies. It is true that there are coloured substances other than those of the aromatic series, but they are either complex bodies, such as murexide (which also has a cyclic structure), or substances such as iodoform, the colour of which is probably due to the mere *presence* of the iodine atoms, rather than to the *linkages* of the atoms in the molecule, and so lies outside the scope of the theories for *organic* compounds in particular.

It was in 1865 that Kekulé brought forward his well-known ring formula to express the constitution of benzene, and it is difficult to over-estimate the importance of this conception. Since that time many slight modifications have been proposed, such as that of Claus (diagonal) and

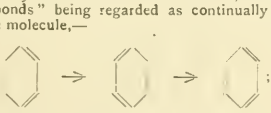


Claus.



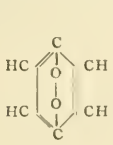
Baeyer-Armstrong.

Baeyer-Armstrong (centric), but these have no particular advantage over the Kekulé formula, which, as originally given, is a *dynamic* and not a static one, the so-called "double-bonds" being regarded as continually revolving round the molecule,—

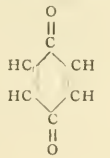


the original reason for this hypothesis being that if the "double-bonds" were fixed, then there would be four di-substitution products of benzene, instead of three, as is actually the case. The importance of this dynamic view in connection with colour theories will be seen later, but it may be as well to state at this point that these theories necessitate a vibration in the benzene molecule. Collie has devised a space formula for benzene, according to which the Kekulé centric, diagonal, and many other suggested formulæ for benzene represent only different phases in the vibration of the molecule.

Soon after Kekulé's epoch-making theory, much work was done on the synthesis of various colouring matters



I.

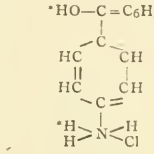


II.

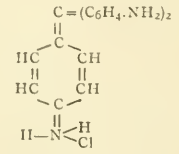
—notably that of alizarin by Graebe and Liebermann—but there is not much to chronicle concerning colour theories till 1888, when Nietzki and Armstrong advocated the quinonoid structure for coloured aromatic compounds. Quinone has the formula $C_6H_4O_2$, and two constitutions have been devised to account for its behaviour—the peroxide formula of Graebe (I.) and the ketonic formula of Fittig (II.).

It seems probable that the substance is tautomeric, but its constitution is usually represented by the latter formula, which is taken as the starting-point of the generalisation that coloured bodies have a quinonoid structure :—

The reason for this theory is best seen by the study of a few characteristic examples. The colour base of pararosaniline is $C{\equiv}(C_6H_4.NH_2)_3{\cdot}{}^{OH}$ and is colourless ; this forms a colourless salt by the addition of one molecule of HCl which has the Formula A.



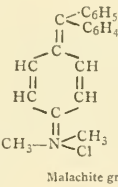
A.



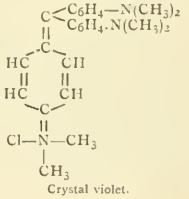
B.

(The asterisks denote the groups which split off to give B).

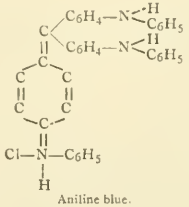
This salt is very unstable, and it readily loses one molecule of H_2O, and gives the brilliant magenta dye (B). In a similar way, other dyes derived from $HO.C{\equiv}(C_6H_5)_3$ are salts formed with elimination of water, and may be given a quinonoid structure ; examples are :—



Malachite green.



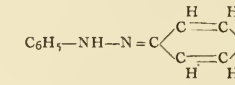
Crystal violet.



Aniline blue.

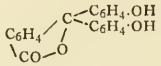
Another set of brilliantly coloured substances is formed by the azo-compounds, many of which are commercially used as dyes. As an example, we may take amidoazo-benzene (aniline yellow). Its synthesis suggests the

formula $C_6H_5—N=N—C_6H_4.NH_2$, but its reactions are just as well expressed by the formula—

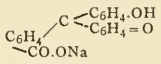


where we again have the quinonoid structure.

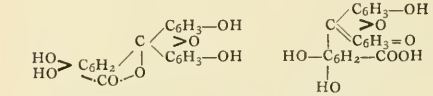
It is a well-known fact that phenolphthalein is colourless in neutral or acid solution, but becomes intensely coloured with a trace of alkali. This is accounted for by the fact that the substance itself is not a true acid, but has a lactone formula,—



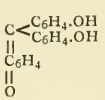
while in the coloured salt the lactone ring is opened out-giving a quinonoid structure :—



Similarly, we have for the fluoresceins the formulæ—

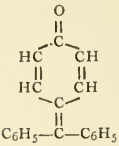


Type of colourless derivative. } Flouresceïn. { Type of coloured derivative.

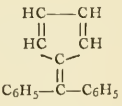


Aurine.

Aurine also forms a hydrochloride, and this according to Baeyer and Villiger (*Berichte*, 1904, lvii., 2848) is also of the quinonoid type, the oxygen being tetravalent as in dimethylpyrone salts and those of other "oxonium" bases. At the same time, these authors bring forward arguments in favour of Fittig's formula for quinone, and they point out how diphenylquinomethane (the parent substance of aurine) only differs from diphenylfulvene by a single carbonyl group :—

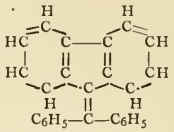


Diphenylquinomethane.

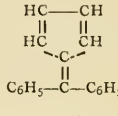


Diphenylfulvene.

The latter is deeper red than the former, and therefore the carbonyl group by itself does not appear to be a chromogen as is often supposed. Baeyer and Villiger account for this by saying that the addition of the carbonyl group causes the five-membered ring to become a six-membered or benzenoid ring, thus weakening the aliphatic nature of the "double bonds," and so causing the molecule to approach more nearly to the type of benzene, with simultaneous loss of colour. This view is at first sight strengthened by the relation between diphenylenediphenylethylene and diphenylfulvene :—



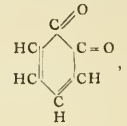
Diphenylenediphenylethylene.



Diphenylfulvene.

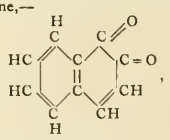
In the former, both the ethylenic double bonds have become part of aromatic rings, and simultaneously the colour has vanished. Baeyer and Villiger, however, offer no explanation of the fact that a solution of diphenylenediphenylethylene is yellow, as is also the molten substance. The explanation of this is probably that the diphenylenediphenylethylene is really coloured, and that the colourless solid is a polymer of it. This of course destroys the value of the relationship, and leaves the whole question still open, but the above facts are worth citing as they show the necessity for great caution when proposing theories of colour. The properties of the above mentioned substances and of bidiphenylene-ethylene are being investigated at present by the author of this paper, in order to shed further light on the subject.

So far consideration has only been given to the paraquinones, of which ordinary quinone is the type. The *simple* orthoquinone—

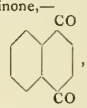


was for long unknown, but it has recently been prepared by Willstätter and Pfannensteil (*Berichte*, 1904, xxxvii., 4744), who isolated it in the form of light red plates.

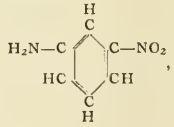
β-Naphthoquinone,—



is far better known, and is also a red crystalline body, the corresponding paroquinone,—



being yellow, like ordinary quinone. This is quite a general fact, the simple paraquinones being yellow and the orthoquinones red. Although the consideration of orthoquinones extends the usefulness of the theory of quinonoid structure, yet there are still many instances where it cannot be applied. For example, the brilliant yellow colour of metanitraniline,—



cannot be accounted for by the usual theory of quinonoid structure. Another weakness of the quinonoid theory in its original form, is that it does not attempt to explain *why* quinonoid bodies should be coloured.

The answer to this question will be discussed in Part II., but before passing on mention should be made of Witt's theory of chromophores, and other similar theories, according to which colour is due to certain chromophoric groups, such as :—

1. $CO-C=C-C=C$
2. $-CO-CO-C=C$
3. $-C=C-CO-C=C$
4. $CO-C=C-CO$

It should be noticed that 1 and 2 contain the same groupings as the orthoquinones, and that 3 and 4 have the same groupings as in paraquinones. Witt, from his investigations of nitrogen compounds has proposed other "chromophores" to account for their colour. Thus, toluylene blue, $N(CH_3)_2-C_6H_4-N=CH-C_6H_3(NH_2)_2$, contains the chromophore $-N=\overset{H}{\overset{|}{C}}-$, which Witt regards as a link between that of rosaniline, $\equiv C-NH$, and that of the azo-series, $-N=N-$. This theory is simply of use to co-ordinate facts, and it does not appear to be very fertile or useful when compared with the other theories of colour.

We have now considered the more or less empirical theories that have been brought forward to "explain" the cause of colour, but it will be seen that none of these are very complete or satisfactory. In Part II. will be considered the recent developments of the subject which tend to explain the true physical meaning underlying the theory of quinonoid structure, and which promise to throw a most important light on the problems of chemical structure in general.

(To be continued).

THE NATURE OF THE NON-ABSORBENT ZONES MADE BY INK BLOTS ON BLOTTING-PAPERS.

By CLAYTON BEADLE and HENRY P. STEVENS.

Although considerable notice has been taken of the non-absorbent zone produced by ink on certain makes of blotting-paper, no systematic attempt has been made to ascertain the *cause* of the non-absorbency of this zone (see Beadle and Stevens, *Paper and Pulp*, Dec., 1904, p. 717).

Throughout this work we have as in former papers used Stephens's blue-black ink as a standard quality, and always from a freshly opened bottle. We consider this as a more practical test than if use had been made of a standard record ink.

When ink, such as Stephens's blue-black ink, is allowed to flow on to a sheet of blotting-paper held horizontally, say in quantities or 0·5 cc. at a time, and when the blot after it ceases to spread is held up to the light, an outer ring or zone will be noticed with several of the best makes of blotting both before and after such blots have been allowed to dry. If after drying such blots fresh ink be drawn across or dropped upon these blots by means of a pen or pipette, the outer zone will be found to have lost its absorbency for ink, although the inner portion still retains its absorbency more or less. The percentage that the width of this zone bears to the total diameter of the blot gives a figure which is fairly constant with given makes of blottings if tested always with the same kind of ink, and this figure since our first published researches has been recognised as a test for absorbency both in this country and in Germany.

As a more accurate means of recording this loss of absorbency (see Beadle and Stevens, *Paper and Pulp*, Dec., 1904, p. 721), we prefer now to express the ratio in relative areas of the non-absorbent zone to that of the total areas of the blot produced. The appearance as well as the width of the zone varies with any given ink for different blottings, or with different inks when applied to any particular make of blotting.

It has been assumed that the gum of the ink is responsible for the production of this non-absorbent zone. If such had been the case, digesting ink blots so produced in warm water in which the gum would dissolve would remove the zone, but finding that the zone was not diminished by this treatment, at least on those blots that had been produced for some time, we looked to the iron salts of the ink as the probable cause of the difficulty. (Communication to the Society of Pulp and Paper Chemists, Nov., 1907).

Before describing the results of our recent work we must first refer to what is now a matter of history. It has long been known to us that certain basic constituents, notably the lime salts contained in the paper, are the cause of certain papers giving a non-absorbent zone.

This matter was fully treated of in our original paper (*Paper and Pulp*, Dec., 1904, p. 723), where we gave the analyses of the constituents of the ash of a number of blottings. We were therefore somewhat surprised to find the following statements on page 184 of the recently published third edition of Herzberg's "Papierprüfung." After describing our zone test and the results of a number of determinations made in the Materialprüfungsamt, Prof. Herzberg discusses the cause of the impervious zone, and refers to question of lime salts in the paper, stating that our view of their primary connection with the impervious zone cannot hold water and may be dismissed *without the need of making anatyses*. He arrives at this conclusion from certain deductions based on a relationship between the ratio of rise and percentage of impervious zone. From an examination of his figures we very much doubt if any such relationship exists, at any rate it is certainly subject to many exceptions, in particular as regards rag papers, where no relation can be traced of the kind mentioned. Thus if we take the table given on p. 182 of Herzberg's "Papierprüfung" and pick out the rag papers and compare them with one another, we obtain the following figures :—

Herzberg's reference number.	Per cent ash.	Mean rise in ten minutes.	Per cent width of zone. Alizarin ink.	Iron-gallic acid ink.	Mean with both inks.
4	1·0	132	7	7	7
5	0·8	121	8	10	9
8	0·8	85	6	10	8
9	2·8	68	1	10	5·5
10	0·8	59	10	12	11
12	3·0	44	1	10	5·5
13	12·8	34	1	10	5·5
14	1·0	31	12	13	12·5

We think that a careful study of the above figures will not reveal any very simple relationship between the mean rise in ten minutes and the percentage width of zone whether the figures for either of the two inks to be taken or the mean of both. Yet according to Herzburg ("Papierprüfung," 3rd edition, p. 183) it usually happens that those papers giving the greatest mean rise yield the widest zones. (It will be seen that in the above table No. 4 giving the greatest rise gives a relatively narrow zone, while No. 14 with the least rise gives the widest zone.) As we have attributed the cause of the zone to a relatively high percentage of basic constituents, in particular lime in the paper, Herzberg arrived at the conclusion that papers giving the greatest mean rise would have the highest percentage of lime, an assumption which he states will not hold water. Having arrived at this conclusion in this curiously roundabout manner, he feels quite satisfied in dismissing our explanation of the cause of the zone without troubling to make analyses which he thinks would be quite unnecessary.

Under these circumstances we feel that it is necessary to refer again to the figures we previously published in *Paper and Pulp*, Dec., 1904, p. 723, showing that those papers examined giving a wide zone contained relatively large proportions of lime, and those giving a narrow zone only traces of lime.

As to wood pulp a sample sheet zoneless-to-ink will yield a blotting also zoneless-to-ink if basic mineral matter be excluded. We have tested reveral samples of wood pulp, and found them zoneless-to-ink. The rate of rise of water in any blotting depends on the *make* of the paper. One of us proved this with commercial English makes. The rate of rise varied as the percentage of air-space; in other words, the greater the sponginess the greater and quicker the absorbent qualities (Clayton Beadle, "The Fibrous Constituents of Paper," *Technics*, vol. i., p. 573). Some materials may be so manipulated in the process of manufacture into paper as to give a high figure for the rate of rise, but at the expense of other important qualities (*i.e.*, felting qualities), but with the same material made into a good felted sheet the rise may be, and often is, much less.

That the formation of an impervious zone is primarily due to the basic constituents of the paper may be shown by a very simple experiment. Take a sheet of blotting giving a non-absorbent zone of considerable area and digest it for a short while in a weak solution of an acid to remove the basic constituents, wash well with distilled water, and dry. The paper will now be found to yield no non-absorbent zone, or, as we may shortly describe it to be, zoneless-to-ink. Soaking in hard water and drying is sufficient to destroy the zoneless-to-ink character of the paper again, or by the use of lime-water a zoneless-to-ink paper may be converted into one giving a wide zone. A number of other basic constituents have been added to zoneless-to-ink paper, giving rise to zones varying according to the amounts added. If a paper containing in addition to lime salts, iron, alumina, and other bases, either as oxides or hydroxides or basic salts, be treated carefully with weak acid so as to remove only the lime salts, the tendency to formation of zone is diminished, but not entirely removed; that which remains is due to bases other than lime.

We think that Prof. Herzberg must admit that these simple experiments confirm in all respects the results of analyes of the ash referred to above, and point to the primary importance of basic substances such as lime in the formation of the impervious zone. If further confirmation were desired, we may state that we are patentees of a process for the production of zoneless-to-ink paper which has been worked successfully in a mill, and is still giving satisfactory results, and that our patent is based on the production of a blotting-paper from which the basic mineral constituents are removed or rendered inactive.

Before proceeding further we may therefore take it as proven that a zoneless-to-ink blotting is free, or practically so, from basic mineral constituents, while a paper giving a zone will be found to contain a larger or smaller proportion of basic substances or bodies capable of neutralising acids, and that the formation of a zone is a quality entirely apart from fibrous constituents or felting qualities, and, furthermore, that the production of zone is a quality entirely apart from bibulous qualities as measured by rate of rise in water.

To investigate the action of iron salts on blotting-paper producing zones we treated a paper known to give a wide ink zone by dropping on to its surface ferric chloride solutions of different concentrations.

(It is worthy of note that the imperviousness of a zone is greater in old blots in comparison with freshly prepared ones, and when testing the width of zone on blots freshly prepared. And again after two and a-half years we have found a distinct increase in the width of imperviousness due to ageing).

It was found that except in the case of very concentrated solutions tested immediately after drying, an impervious zone or ring was produced on the margin of the blot. The loss of absorbency produced by blots of very strong ferric chloride solution immediately after drying in an oven, is to be ascribed merely to a dried residue of a high concentration being produced in the paper, and has nothing to do with the impervious zone above referred to. This loss of absorbency, due to high concentration, disappears when the blots take up moisture from the atmosphere.

If a zoneless-to-ink paper is treated as above described with ferric chloride solutions of different concentrations, it is found in all cases to be zoneless to ferric chloride. If, however, the same paper be artificially loaded with carbonate of lime it will produce an impervious zone with ink, and it will be found that as the concentration of the ferric chloride solution is reduced, a zone is produced which within certain limits varies in width inversely as the concentration of the ferric chloride solution. When the concentration of the ferric chloride is reduced to that of the iron salts normally contained in ink, the zone is at least as wide as the zone produced by ink itself. If now any commercial paper be chosen which is known to produce a zone with, say, Stephens's blue-black ink, it will also be found to produce a zone with dilute ferric chloride solution, and the area of the zone so produced will vary with the concentration of the ferric chloride solution.

When ferric chloride blots so produced are dried, and ink is applied to them, it will be found that both the inside and outside of the zone is pervious to ink, whereas the zone itself is impervious, corresponding in this respect to a zone produced by an ink blot similarly dried down and tested. The ferric chloride blots will be found to possess the colour of ferric chloride in that portion of the blot surrounded by the zone, but the zone itself will have the buff colour of ferric hydroxide or basic ferric salt.

When either ferrous or ferric sulphate, with or without the addition of sulphuric acid, is applied to a blotting-paper in a similar manner to the above, it will be found that these salts behave in a similar manner to ferric chloride.

In the case of dilute ferrous sulphate with a small addition of sulphuric acid, which more or less represents the condition of iron in freshly made ink, the effect produced well illustrates the formation of a basic ferric compound or salt in that part of the paper which ultimately becomes a non-absorbent zone. On allowing 0·5. cc. of such a solution to spread in the form of a blot on a zoneless-to-ink blotting-paper, and allowing to dry no zone effect is produced on the paper. If, however, the same experiment be made with a blotting which gives an ink blot with a zone, it will be noticed that as the wetness ceases to spread a change of colour takes place round the outer edge, and when dry there is found to be a buff-tinted impervious zone with a *colourless* and absorbent interior portion. In the case of a blot made with a *neutral* solution of ferrous sulphate, the interior portion is partially non-absorbent.

If, now, with one or other of the above salts we are correct in attributing the non-absorbency of the zone to ferric hydroxide or basic ferric compound, treatment of the blot so produced in water would remove the soluble iron salts from the interior of the blot and leave the insoluble iron in the zone.

This was found to be the case. Thus, a ferric chloride blot was produced, dried down and digested in hot water for the removal of the soluble iron salts, and again dried and tested. It was found that the zone was not removed, and remained impervious, whereas that portion enclosed by the zone had lost its iron salts.

To test this point further a blot was made in a similar manner, but not dried down before immersion in water. Even under these circumstances a non-absorbent zone was produced which withstood the digestion with water.

The increase of the non-absorbent zone due to dilution can be demonstrated by making a small concentrated blot, say, of ferric sulphate, to the centre of which is applied, drip by drip, distilled water from the nozzle of a wash

bottle. The original blot may have given little or no zone, but as the blot already formed is caused to spread the zone is increased, and is rendered visible by the appearance of reddish hydroxide or basic ferric salt, which after drying and testing with ink is found non-absorbent, whilst the interior of the blot retains its absorbency.

When a blot is produced by ferric chloride of an intermediate concentration (say, 15 per cent), which on first drying and testing shows a visible and non-absorbent zone, the same zone is found to have wholly or partially disappeared in about twenty-four hours, due to the fact that the ferric chloride being hygoscopic absorbs sufficient moisture to cause it to go into solution, and so dissolve the freshly deposited ferric hydroxide. With solutions of ferric chloride of lower concentrations, such as those which do not produce any visible hygroscopic effect, and remain dry to the touch, the visible and non-absorbent zone remains permanent.

The loss of zone with intermediate concentrations when using ferrous sulphate, even with the addition of a small amount of acid, is not noticeable. This we attribute to the fact that the deposits are non-hygroscopic.

The reason of the deposition of the ferric hydroxide or basic salt from the soluble iron salts is not to be accounted for as a process of dissociation, because these iron salts do not show a non-absorbent zone, except in contact with paper containing certain basic constituents capable of depositing ferric hydroxide or basic salts by combination with the acid radicle. When a few drops of soluble iron salts are placed on such a paper, at first the acid constituents of the blot are in excess, but as the blot spreads the basic constituents of the paper begin to predominate, from which point outwards ferric hydroxide is deposited and the non-absorbent zone is produced. It consequently stands to reason that the less concentrated the iron salt the sooner the basic constituents of the paper begin to predominate, and the wider the zone produced.

Ferric hydroxide or a basic salt being, as it were, deposited *in situ*, and probably in a colloidal condition, is capable of sizing the paper and so rendering it ink-proof.

To ascertain whether the iron of the ink behaves in a similar manner, and accounts for the production of the non-absorbent zone, we took some ink blots produced by discharging 0·5 cc. of Stephens's blue-black ink on a paper giving rise to a wide zone. Portions of blots so produced after drying were bleached by immersion in strong bleaching-powder solution, which discharges the colouring matter of the ink, leaving the iron as a residue in the paper.

If, now, a blot so bleached out, and after immersion in water be held up to the light, it will be seen that the centre of the blot, as well as the body of the paper itself, is thoroughly wetted through and transparent, whereas the non-absorbent zone remains opaque and of about the same degree of opacity as the dry blotting-paper in consequence of its refusal to absorb water. Figure 7 shows a print produced from a blot while still wet after bleaching out the colouring matter of the ink. This photograph is a *negative* produced by contact with *wet* blotting-paper, and taken by transmitted light to show the relative wetting qualities of the zone and the body of the paper. The zone remains white because when wetted it remained as opaque as a dry sheet. The interior of the blot is in reality as transparent as the body of the paper, but does not appear so on the photograph, because the yellow colour of the iron salt it contains intercepts some of the actinic rays.

Viewing one of these wetted bleached-out blots by reflected light, the non-absorbent zone will appear as an incrustation. For some reason or other the surface of the zone does not frequently show the characteristic brown colour until the blot is dried down by heat, when it begins to develope, but the brown colour can be produced by moistening with ammonia.

Before drying the colour may be described as a dirty white, probably due to some basic salt, which partially decomposes on drying down or on treating with a base with the production of ferric hydroxide.

There is something peculiar about this deposit producing the non-absorbent zone which we have not yet fully accounted for, and which we are still investigating.

The non-absorbent zone of the bleached-out ink blot is still as impervious to ink as before bleaching out.

If the bleached-out product after prolonged soaking in water is brought upon a glass plate whilst still wet, and ink applied on either side of the zone, the ink flows on either edge without passing over it, thus showing the zone is still non-absorbent even after bleaching and prolonged wetting.

If a bleached-out blot after washing and drying is placed for a time in a dilute solution of potassium ferrocyanide to which is added a few drops of hydrochloric acid, the interior immediately developes a blue colour, whereas the zone retains its yellow tint and remains unacted upon, thus showing the difference in the condition of the iron residue from the ink contained in the interior of the blot, and that constituting the impervious zone.

Thinking that there would be a difference in the solubility of the iron contained in the interior of the blot as compared with that contained in the zone, a bleached-out blot was treated with a 10 per cent HCl solution in the cold for a few minutes, and then washed. The iron in the interior of the blot was found to have gone into solution, whereas the iron contained in the zone was still unacted upon. This is further rendered evident by subsequently developing the above mentioned blot in potassium ferrocyanide.

If now a part of the same blot be again treated with strong hydrochloric acid, the zone gradually loses its non-absorbent nature, first of all becoming of the colour of ferric oxide, and then developing a blue colour with potassium ferrocyanide. If now the portion of the zone which has been converted into Prussian blue by this process is dried and tested with ink, it is found to be pervious, whereas that portion not so treated remains impervious.

Thinking that further light might be thrown upon the nature of the zone if the proportion of the iron contained in the interior and zone of the blot were separately determined, we took two blots produced on paper giving a wide zone, one of these blots A was slightly moistened so as to admit of the interior absorbent portion being detached from the exterior non-absorbent zone, and the body of the paper surrounding the zone was also moistened in order that it might be separated in the same manner. By this means a ring consisting of the non-absorbent zone was completely detached from the interior of the blot and the body of the paper, so that each could be separately examined.

The zone and interior of blot A were dried, weighed, ignited, and the iron in the ashes of each determined.

Zone of Blot A contained	..	4·6 per cent Fe.
Interior of Blot A contained	..	1·5 do.

Thus it will be observed that the non-absorbent zone which from its colour does not appear to contain anything like so much ink as the interior portion, as a matter of fact contains three times the percentage of iron as compared with the interior. It should be observed that on drying, and before ignition, the ring weighed 0·195 grm., and the interior 0·329 grm.; therefore the ring as detached constituted 37 per cent by weight of the blot and the interior 63 per cent.

We thought it advisable to take a similar blot, and to digest it for some time in hot water before detaching the ring from the interior so as to remove all the soluble constituents of the ink. This was accordingly done, and the zone separated from the interior as above described. The zone and the interior on drying were found to weigh as follows:—

Blot B.

Zone	0·169	grm.
Interior	0·249	„

The total weight of the blot so extracted was therefore

0·418 grm. as against the total weight of blot A unextracted of 0·524 grm.

The mean diameter of blot A was found to be 40·0 mm., the mean diameter of blot B to be 40·8 mm., the blots having been produced with 0·50 cc. of ink in each case. It may be assumed, therefore, that extraction with water reduced the weight of the blot by 20 per cent.

The ring and interior of extracted blot B were ignited and the iron determined in the ash, yielding the following figures expressed on the weight of the extracted blot.

Zone .. .. .. 4·6 per cent Fe.
Interior .. .. 2·0 „ „

If, however, the amount of iron found be expressed on the non-extracted blot in order to compare it with blot A, the following figures are obtained:—

Zone .. .. .. 4·0 per cent Fe.
Interior .. .. 1·5 „ „

It is evident, therefore, that the amount of iron contained in the blot is for the most part insoluble in water, and that the iron tends to migrate to the exterior of the blot during the formation of the impervious zone. It also appears that the interior of the blot contains iron easily soluble in dilute hydrochloric acid (even after bleaching out the tannic or gallic acid), whereas the iron of the zone is much less soluble, so much so that the one can be separated from the other by digestion in weak acid.

If that portion of the blot inside the zone be wetted and tested with litmus-paper, it is found to have a strong acid reaction, even when the blot is several years old, while the zone itself and the body of the paper outside the zone is without action on litmus-paper.

If the interior of the blot is cut out and placed in methyl orange solution it will be found to be strongly acid, while the zone is neutral and the body of the paper basic.

We think that we have sufficiently proved that the impervious zone produced by contact of writing ink with certain kinds of blotting-paper is due to the decomposition and deposition of the iron salts contained in the ink by certain basic constituents of the paper giving rise to the formation of ferric hydroxide, probably in colloidal form or other basic salts which filling the pores of the paper render it resistant to ink.

THE OXYGEN EQUIVALENT OF COCOANUT OIL.

By T. R. HODGSON, B.A., A.I.C.

The process used for the determination of the "oxygen equivalent" of cocoanut oil is that described in the previous paper, and again consists in the oxidation of the acids obtained after saponification and acidification.

Twenty samples of cocoanut oil were examined; they were all obtained in Birmingham, were all of the commercial variety, and were not subjected to any special purification. The following results were obtained:—

Sample.	$K_2Mn_2O_8$ used. Cc.	Sample.	$K_2Mn_2O_8$ used. Cc.
A.	25·0	L.	24·8
B.	21·6	M.	21·8
C.	21·8	N.	21·7
D.	26·8	P.	21·7
E.	21·8	Q.	21·8
F.	18·0	R.	21·8
G.	18·8	T.	21·7
H.	21·6	V.	21·2
I.	21·2	X.	21·7
K.	21·8	Z.	21·7

The number of cubic centimetres of tenth-normal potassium permanganate solution used multiplied by 4 gives the "oxygen equivalent." This, in the case of cocoanut oil, varies considerably, viz., from 72·0 to 107·2.

Sample.	Oxygen. equivalent.	Sample.	Oxygen equivalent.
A.	100·0	L.	99·2
B.	86·4	M.	87·2
C.	87·2	N.	86·8
D.	107·2	P.	86·8
E.	87·2	Q.	87·2
F.	72·0	R.	87·2
G.	75·2	T.	86·8
H.	86·4	V.	84·8
I.	84·8	X.	86·8
K.	87·2	Z.	86·8

As will be seen from the above numbers, the variation is very considerable, but even the highest number obtained is very much lower than that of butter fat.

The average number obtained with the twenty samples examined is 88·66, leaving a difference of 80·54 between the average "equivalent" of the oil and that of butter fat.

The variation in the equivalent in the case of cocoanut oil is probably due to variation in the quality of the oil, as the price of the different samples varied considerably, ranging from 4d. to 2s. 8d. per pound. The influence of time on the oxidation is, as in the case of butter fat, variable up to about thirty minutes, but from thirty minutes up to one hour no oxidation seems to occur.

Time. Minutes.	$K_2Mn_2O_8$ used. Cc.	Oxygen equivalent.	
5	19·2	76·8	1·6
10	19·6	78·4	1·2
15	19·9	79·6	0·4
20	20·0	80·0	7·2
25	21·8	87·2	
30	21·8	87·2	
35	21·8	87·2	
40	21·8	87·2	
45	21·8	87·2	
50	21·8	87·2	
55	21·8	87·2	
60	21·8	87·2	

The numbers given above show that there is no regular increase in the equivalent; the large increase between twenty and twenty-five minutes is remarkable.

In my next paper the results of this and the previous paper (Chemical News, vol. xcvi., p. 273) have been applied to mixtures of cocoanut oil and butter fat in known proportions.

Analytical Department,
University of Birmingham.

Action of Sodium Dioxide and Barium Dioxide on Gold: Aurates.—Fernand Meyer.—When precipitated gold is added to fused sodium dioxide in a nickel crucible, nickel oxide is formed and some gold remains unaltered, while the solution obtained by adding water contains sodium aurate. Barium aurate can be prepared similarly. The action of sulphuric acid on an aurate gives auric acid. If auric acid is allowed to stand over sulphuric acid *in vacuo* and in the dark, its formula is found to be $Au_2O_3.3H_2O$. Sodium aurate may be prepared for analysis by adding a solution of soda to auric acid in absence of the carbon dioxide of the air. Strontium and calcium aurates may be prepared similarly. The formulæ of the compounds are $(AuO_2)_2Na_2$, $(AuO_2)_2K_2$, $(AuO_2)_2Ca$, $(AuO_2)_2Sr$, $(AuO_2)_2Ba$. They are stable on heating if dry. In solution they are decomposed by light and heat, the residue being violet-black Au_2O, which is soluble in hydrochloric acid. Sulphur dioxide reduces them to metallic gold.—*Comptes Rendus*, cxlv., No. 20.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21st, 1907.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

The President announced that the Society has received a portrait of Faraday and Daniell from Professor Meldola, and a silver medal from the Société Chimique de France, struck in commemoration of the recent Jubilee celebration.

Certificates were read for the first time in favour of Messrs. John Arthur Carpenter, B.A., New College, Oxford; Cyril Dickinson, B.Sc., F.I.C., Abbotsford, Holycroft Avenue, Hampstead, N.W.; Edward Mortimer Eagles, M.A., 5, Winsham Grove, Clapham Common, S.W.; Robert Cecil Gale, 38, Scarsdale Villas, Kensington, W.; George Neville Pingriff, B.A., 39, Hall Road, Handsworth, Staffs.; William Bayliss Shaw, Lonsdale House, Walsall; Harry Jackson Unwin, Market Place, Clay Cross, nr. Chesterfield; Herbert Walker, Whyttington, Station Road, Wealdstone, N.W.; Joseph Henry Williams, 27, Canbury Avenue, Kingston-on-Thames.

Certificates have been authorised by the Council under By-law 1. (Par. 3) in favour of the following:—Edward Henry Croghan, care of Messrs. H. Eckstein and Co., P.O. Box 149, Johannesburg; Charles Thomas Foreman, Jamalpur, E.I.R., Bengal.

Of the following papers, those marked * were read:—

*225. "*Emulsions.*" By Spencer Pickering.

Paraffin oil, when churned with solutions of soap, glue, starch, albumin, &c., forms an emulsion which rises, like cream, to the surface of the excess of water, and contains from 65 to 82 per cent by volume of the oil. Close-packing of uniform globules would give an emulsion containing 74 per cent. The percentage of oil can be increased to 99 per cent, the emulsion then being practically solid. Emulsification seems to depend on the separation from the liquid of very minute solid particles which are attracted by, and surround, the oil globules, thus preventing them from coalescing. Any precipitated substance which is sufficiently finely divided will act as an emulsifying agent, but, after becoming agglomerated by drying, it loses this property. The basic sulphates of iron and copper are conspicuously good emulsifiers, and, when they are used instead of soap, it is possible to mix with the emulsions substances which could not be added if soap had been used; for example, sodium hydroxide. Solids which are not sufficiently fine grained to make true emulsions with oil, will sometimes make quasi-emulsions, in which the oil globules are merely entangled with the solid particles. In this case, dilution with water separates the oil from the solid, which is not the case with true emulsions.

Discussion.

Dr. Lewkowitsch thought that all the phenomena mentioned by the author could be best explained by the colloidal state of the substances employed. He would therefore take exception to the explanation that the paraffin oil emulsified the soap solution, and would prefer to say that the soap solution emulsified the paraffin oil. Soap solutions were typical colloids, easily gelatinisable even in dilute solutions, and it was also well known how disconcerting soap solutions were once they had formed an emulsion with other substances, notably vegetable or mineral oils. The percentage (97) of paraffin oil in the emulsion shown appeared very high, and he therefore asked how much water and how much soap, presumably soft soap, were in the remaining 3 per cent. Soap solutions emulsified, not only paraffin oils, but also alcohol, and notably very large amounts of water.

The ferric sulphate and also the copper salt mentioned by the author were known to occur in the colloidal state, and therefore their property of forming emulsions would explain the phenomena referred to. The experiments shown with the emulsions produced by soap would fall in well with that explanation. On adding hydrochloric acid, the soap was decomposed with the formation of free fatty acids. These, at any rate those formed in the given case, were not colloids, and therefore the emulsion was "broken" at once, and water separated, the fatty acids remaining dissolved in the petroleum. The fact that caustic soda "broke" the emulsion was also easily explained, as caustic soda "salts out" soaps; that is, precipitates them from their colloidal solution, and therefore water must separate out again. That in the experiment with lime no emulsion was formed could also be readily explained by adopting his view, for under the given conditions lime would not behave like a colloid.

Mr. J. Castell-Evans thought that surface-tension had a great deal, if not all, to do with the formation of emulsions, and that many finely-divided substances may be found which will induce the formation of emulsions of petroleum and water. He instanced a case, falling within his own personal observation, in an attempt at "oil concentration" of the metalliferous contents of some calcined tailings. These tailings consisted largely of ferric oxide, and, after calcination, had been "weathered" for many years. On shaking up with water and mineral oil of about 0·89 sp. gr., the silicious matter, as expected, sank to the bottom of the cylinder; so also did the coarser particles of ferric oxide, whilst the finer particles of the oxide remained in the oil, forming apparently a true emulsion. This "emulsion" did not make the sides of the cylinder oily, and remained persistent for many months. The coarser particles of the oxide did not present a sufficiently large surface, in proportion to their mass, to be retained by the petroleum.

Dr. Borns inquired whether the author had succeeded in obtaining any emulsions of oil and pure water. K. Beck (*Zeit. Phys. Chem.*, 1907, lviii., 409) had found that the viscosity of water was not affected when the water was churned with oil. When he prepared an emulsion of oil and water by rubbing the oil with some gum arabic in a mortar and adding water, however, the viscosity of the water was increased.

The President suggested that the suspended particles in an emulsion may be similarly electrified, and so repel each other and fail to coalesce. No doubt this phenomenon is closely connected with surface-tension phenomena. The addition of electrolytes may possibly discharge the electrified particles and cause coalescence.

Mr. Pickering, in reply, stated that the strongest emulsion which he had obtained contained only 1 per cent of a 1 per cent soap solution. The action of soap as an emulsifying agent was very uncertain, but that was not the case with insoluble emulsifiers. Such colloids as he had tried did not emulsify, but, on the contrary, became gelatinised. The basic sulphates were clearly not colloids; the particles composing them could be seen under the microscope. No doubt surface-tension played an important part in emulsification, but that offered no explanation of the phenomenon. Electrolytes, as such, had no effect on emulsions.

*226. "*Aromatic Azoimides.* Part III. *The Naphthylazoimides and their Nitro-derivatives.*" By Martin Onslow Forster and Hans Eduard Fierz.

For the purpose of studying further the triazo-group, and the conditions under which its properties are influenced by other groups, azoimides of the naphthalene series have been examined.

α-Naphthylazoimide, $C_{10}H_7{\cdot}N_3(\alpha)$, melts at 12°, and does not yield hydrazoic acid when heated with alcoholic potash; the *2-nitro-* and *4-nitro-*derivatives, melting at 103—104° and 99° respectively, are resolved into the corresponding nitronaphthols and hydrazoic acid. The heteronucleal *5-nitro-* and *8-nitro-1-naphthylazoimides*, melting at 121° and 130—131° respectively, do not furnish hydrazoic acid.

β-Naphthylazoimide, $C_{10}H_7 \cdot N_3$(3), melts at 33°, and like the heteronucleal *5-nitro-* and *8-nitro-2-naphthylazoimides*, melting at 33·5° and 108° respectively, does not give hydrazoic acid. *1-Nitro-2-naphthylazoimide*, melting at 116—117°, is characterised by the readiness with which it loses nitrogen when heated, passing into the peroxide of β-naphthaquinonedioxime, which is also obtained, but less readily, from the 2-nitro-1-naphthylazoimide; the 1-nitro-2-naphthylazoimide yields hydrazoic acid when heated with alcoholic potash.

*227. "*The Triazo-group.* Part I. *Triazoacetic Acid and Triazoacetone* (*Acetonylazoimide*)." By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

The interesting properties displayed by the triazo-group $-CH \cdot N_3$ / $-CO$ when occurring in the complex, have led the authors to prepare the simplest typical compounds of this class, triazoacetic acid and triazoacetone.

Triazoacetic acid, $N_3 \cdot CH_2 \cdot CO_2H$, is a colourless substance, which crystallises in lustrous, transparent, hygroscopic plates, melting at 16°; it is a strong acid, has a faint odour recalling that of butyric acid, but much less pungent, and when dropped on a hot iron plate detonates with a moderate explosion, taking fire. The *silver* salt, $C_2H_2O_2N_3Ag$, crystallises from boiling water in lustrous colourless needles, which decompose slowly when exposed to light; the *ethyl* ester, $C_4H_7O_2N_3$, is a limpid colourless oil, which boils at 45° under 2 mm. pressure, and has a very faint odour recalling chloroform rather than ethyl acetate. *Triazoacetamide*, $N_3 \cdot CH_2 \cdot CO \cdot NH_2$, crystallises from benzene in long lustrous colourless needles, melting at 58°.

The derivatives of triazoacetic acid are much more sluggish in their reaction with concentrated sulphuric acid than is usually the case among compounds containing the triazo-group; when shaken vigorously with the acid, however, nitrogen is liberated. A neutral solution of potassium triazoacetate may be boiled without undergoing change, but in presence of free alkali, two-thirds of the azidic nitrogen is eliminated in the elemental form, the remainder separating as ammonia.

Triazoacetone (*acetonylazoimide*), $N_3 \cdot CH_2 \cdot CO \cdot CH_3$, is a colourless limpid oil, which boils at 54° under 2 mm. pressure; the freshly prepared substance has a very faint odour recalling that of chloroacetone, but much less pungent, spontaneously acquiring a suggestion of carbylamine after a few days. It is moderately soluble in water, and when shaken with dilute aqueous potash briskly liberates nitrogen, gas evolution being almost explosive when a 40 per cent solution of alkali is used; dropped on a hot iron plate, the substance detonates feebly, taking fire, and concentrated sulphuric acid decomposes it immediately. The *semicarbazone*, $C_4H_8ON_6$, crystallises from hot water or absolute alcohol in long lustrous needles, which melt without evolving gas at 152°.

The triazo-derivatives of acetone and acetic ester were prepared by the action of sodium azide on the respective chloro-compounds. The authors are engaged in a study of the products obtainable from salts of hydrazoic acid, and the halogen derivatives of acids, esters, ketones, aldehydes, and alcohols.

DISCUSSION.

Dr. KEANE asked whether Dr. Forster had examined the decomposition products of the azoimides of acetic acid and ethyl acetate when two-thirds of the total nitrogen was eliminated, and if so, whether imide derivatives of the aldehydes were obtained as in the case of the camphoryl-azoimide?

Dr. FORSTER replied that these compounds were being investigated.

*228. "*Studies of Dynamic Isomerism.* Part VII. *Note on the Action of Carbonyl Chloride as an Agent for Arresting Isomeric Change.*" By THOMAS MARTIN LOWRY and EGBERT HOCKEY MAGSON.

Labile solutions of nitrocamphor, in which isomeric change has been suspended, have been prepared (1) accidentally by dissolving nitrocamphor in chloroform, and (2) deliberately by adding acid to the solvent chloroform. In the latter case, the solutions acquired a powerful odour of carbonyl chloride, and there can be no doubt that this is the efficient agent in arresting isomeric change in chloroform solutions.

By means of this new agent, it is possible to arrest the isomeric change of nitrocamphor in other solvents. Thus a solution in benzene and N/10,000 carbonyl chloride, when stored in a quartz flask, showed a change of rotatory power of only 1·4° in twenty-five days, whilst a solution to which no carbonyl chloride had been added showed a similar change in four hours. In the same way, the velocity of isomeric change in ether was reduced to one-twentieth by the addition of N/10,000 carbonyl chloride, but no retardation was produced by the addition of acetic anhydride to acetic acid.

*229. "*The Electrometric Determination of the Hydrolysis of Salts.*" By HENRY GEORGE DENHAM.

The author has measured the hydrolysis of salt solutions with the hydrogen electrode. The E.M.F. of the cell, Pt_{H_2} | salt solution | saturation sol. of NH_4NO_3 | calomel electrode, was measured, and from this the concentration of the hydrogen ion was calculated.

A redetermination of the hydrolysis of solutions of aniline, chromium, and aluminium salts gave results agreeing well with those obtained by Ley (*Zeit. Phys. Chem.*, 1899, xxx., 193; Bruner, *Ibid.*, 1900, xxxii., 133; Bredig, *Ibid.*, 1894, xiii., 289, and Bjerrum, *Ibid.*, 1907, lix., 336). In the case of the green chromium sulphate, the results obtained point to the conclusion that the equation given by Recoura (*Ann. Chim. Phys.*, 1895, [7], iv., 494) for the conversion of the blue sulphate into the green is not valid, but that the acid formed is produced through hydrolysis, and its amount depends only on the concentration and the temperature of the solution.

In the case of the salts of zinc, magnesium, thorium, cobalt, and nickel, peculiar variations in the hydrogen ion concentrations have been noticed from day to day. The most probable explanation of this appears to be that the hydrolysis of these salts lead to heterogeneous systems, in which the second phase (hydroxide or basic salt) is present in a colloidal form.

230. "*The Interaction of Metallic Sulphates and Caustic Alkalis.*" By SPENCER PICKERING.

Alkalis, added to solutions of various metallic sulphates, precipitate a definite basic sulphate, except in the case of manganese and magnesium, where the hydroxide is precipitated. After the precipitation is complete, the further addition of alkali converts the basic sulphate either into another, sometimes consecutively into two other, more basic products (for example, copper and nickel), or into the hydroxide (aluminium). When one of the stronger alkalis (potash, soda) is used in excess, the product is probably always the hydroxide, but in the case of lime this does not appear to be so, at any rate not with the sulphates of copper and nickel (see the following communication). In every case examined, different alkalis have given the same results as regards the basicity of the sulphates precipitated by them in each particular case. The existence of the following eleven basic sulphates has been established in this way; the predominance of 5 as the coefficient of equivalents of metallic oxide present is very noticeable. Those marked with an asterisk are the ones formed when the whole of the metal has been precipitated from the solution; the others are products of the action of further quantities of alkali: $5NiO,3SO_3$*, $5NiO,2SO_3$, $5Al_2O_3 \times 2SO_3$*, $4CuO.SO_3$*, $4CoO,SO_3$*, $4CdO,SO_3$*, $5CuO,SO_3$, $5NiO,SO_3$, $5ZnO,SO_3$*, $10CuO,SO_3$, $10FeO,SO_3$*.

231. "*The Chemistry of Bordeaux Mixture.*" By SPENCER PICKERING.

The substances formed on the addition of lime to copper

sulphate, as in the preparation of Bordeaux mixture, are dependent on the proportions of lime used, and may be either—

(1) $4CuO,SO_3,0{\cdot}06CaSO_4$;
(2) $5CuO,SO_3,0{\cdot}25CaSO_4$;
(3) $10CuO,SO_3,1{\cdot}3CaSO_4$;
(4) $10CuO,SO_3,4CaO,SO_3$;
(possibly 5) $10CuO,SO_3,10CaO,SO_3$;
or (6) $CuO,3CaO$;

that present in most cases probably being (4).

The fungicidal action of Bordeaux mixture seems to depend on the liberation of normal copper sulphate by the action of carbon dioxide on the basic sulphate. The action begins only after a certain lapse of time, the basic calcium sulphate having to be decomposed before the basic copper sulphate is attacked. By using only sufficient lime to form $4CuO,SO_3$, the presence of basic calcium sulphate and the consequent delay in the action is avoided; in addition to this, the amount of normal copper sulphate liberated (for a given amount of copper sulphate taken) and the insecticidal value of the mixture will be two and a-half times as great as when it consists of $10CuO,SO_3,4CaO,SO_3$.

The basic sulphates, when precipitated by lime in presence of excess of sodium sulphate, contain sodium sulphate as well as calcium sulphate; the formula of the most basic sulphate is $10CuO,SO_3,(Na_2,Ca)SO_3$. When precipitated by soda, they contain no appreciable amount of sodium sulphate, unless a large excess of the latter is present in the liquid.

Nickel sulphate with lime gives a basic sulphate containing a very little calcium sulphate, but, if the lime is at all times in excess, the basic sulphate is deprived of most of its acid, the precipitate consisting essentially of a double oxide.

232. "*The Alcohols of the Hydroaromatic and Terpene Series.* Part I. *Resolution of the Alcohols into their Optically Active Components and the Preparation of the Borneols.*" By Robert Howson Pickard and William Oswald Littlebury.

An alternative method to that of the authors' (*Proc.*, 1906, xxii., 71) for the resolution of racemic alcohols was described. The alcohol is combined with phthalic or succinic anhydride, and the resulting acid ester resolved by *l*-menthylamine or other strong optically active base. The optically active acid ester thus obtained is readily hydrolysed and yields the active alcohol in a pure state.

l-Borneol was purified by three independent methods and found to have $[\alpha]_D -37{\cdot}9°$ in toluene solution. *d*-Borneol was obtained from the reduction products of camphor by (i.) treatment with zinc chloride in benzene solution, followed by (ii.) conversion in the hydrogen phthalate and purification by means of the *l*-menthylamine salt. It then has $[\alpha]_D +37{\cdot}8°$ in toluene solution.

*iso*Borneol (from camphene) was converted into the hydrogen phthalate and resolved by means of *l*-menthylamine and cinchonine. The *iso*bornyl hydrogen phthalates have $[\alpha]_D \pm 76{\cdot}8°$ in chloroform solution, and when hydrolysed readily yield the pure *iso*borneols, which have $[\alpha]_D \pm 34{\cdot}3°$ in ethyl-alcoholic solution. The identity of Haller's *iso*camphols (obtained by reduction of camphor), which had $[\alpha]_D \pm 32{\cdot}9°$ in ethyl-alcoholic solution, with the inactive *iso*borneol from camphene has long been assumed. The results described may be taken as proof of this, although it is probable that the product obtained from "camphene" contains other substances beside *d*- and *l*-*iso*borneol.

233. *The Electrolytic Preparation of Disulphides.* Part I. *Dibenzyldisulphide and Diethyldisulphide.*" By Thomas Slater Price and Douglas Frank Twiss.

The electrolysis of the alkyl thiosulphates (compare *Proc.*, 1906, xxii., 260), which are used to prepare the disulphides, was originally performed in a beaker, without any diaphragm between the anode and the cathode, and the formation of disulphides was assumed to be due to the decomposition of the discharged anions, according to the equation $2R{\cdot}S_2O_3 \quad R_2S_2+2SO_3'$.

Subsequent experiments, however, with divided cells, have proved the formation of disulphide to be due to the reaction of the alkyl thiosulphate anion at the cathode, according to the equation $2R{\cdot}S_2O_3' + 2H = R_2S_2 + 2HSO_3'$.

The best yield of disulphide is obtained by using a low current density, a concentrated solution, and current in excess of that theoretically required; the addition of sodium carbonate or bicarbonate to the electrolyte is also advantageous.

Although the pure alkyl thiosulphate compounds were used in the earlier experiments, it has been found quite satisfactory to electrolyse the mixture obtained by heating together sodium thiosulphate and the organic halide in aqueous-alcoholic solution; a divided cell is then used.

The bearing of the above results on the constitution of sodium thiosulphate was discussed, since Gutmann, in a series of recent papers (*Ber.*, 1905, xxxviii., 1728 and 3276, &c.), favours the constitutional formula $O{=}S{<}^{S}_{O}{>}S(ONa)_2$ in place of the usually accepted formula $SO_2(ONa)(SNa)$. It was shown that the former formula is not satisfactory, and that all Gutmann's results are in accordance with the latter.

234. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part XI. *Ethyl Tartrate in Aliphatic Halogen Derivatives.*" By Thomas Stewart Patterson and David Thomson.

The rotation of ethyl tartrate has been determined in methylene chloride, carbon tetrachloride, ethylene chloride, ethylidene chloride, acetylene tetrachloride, bromoform, ethyl bromide, ethylene bromide, acetylene tetrabromide, methyl iodide, methylene iodide, and ethyl iodide at various temperatures and concentrations. The values found were compared with those for molecular solution-volume. To some extent an inverse relationship holds between these variables. In all the solvents under consideration, the rotation of the dissolved ethyl tartrate is depressed below that of the homogeneous ester, whilst, on the other hand, the molecular solution-volume becomes greater than the molecular volume. Amongst the individual data also an inverse proportionality often obtains, but a correlation between the two variables cannot be traced through all the solvents examined, since exceptions are both numerous and important.

235. "*The Interaction in Solution of Ferrous Sulphate and Copper Sulphate.*" By Henry Russell Ellis and William Henry Collier.

When ammonia is added to copper sulphate solution, the distinctive blue colouration is not obtained or is rendered indistinct if ferrous sulphate is present.

If excess of ferrous sulphate is present, no colouration is produced, whilst the iron is precipitated as ferrous and ferric hydroxides; the solution contains cuprous compounds, and a small quantity is present in the precipitate. The production of the ferric hydroxide is brought about by the oxidising action of the compound $CuSO_4,5NH_4OH$, and the amount of oxidation is proportional to the amount of this substance present.

Complete oxidation is brought about when both the copper and ammonia are present in excess.

The authors have been able to oxidise the whole of the iron in a few minutes in the cold by using the proportions $10NH_4OH,CuSO_4$, and $\frac{1}{2}FeSO_4$. Solutions of ferrous sulphate, on boiling, become hydrolysed, giving an acid solution.

No action takes place between ferrous sulphate and copper sulphate solutions in the cold, but, on boiling, the copper sulphate slowly oxidises the ferrous hydroxide produced by hydrolysis.

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.

LONDON SECTION.

Ordinary Meeting, December 2nd, 1907.

Mr. R. J. FRISWELL in the Chair.

"*The Estimation of Naphthalene in Coal-gas and Spent Oxide of Iron.*" By C. J. DICKENSON-GAIR.

The methods of estimation given in the paper are as follows :—

The Acetic Acid Method.—300 or 400 cc. of acetic acid solution are placed in two Dreschel bottles coupled with a third bottle, containing picric acid solution as a catch. About 10 cubic feet of the coal-gas are passed through, and the contents of the bottles then mixed with 500 cc. strong picric acid solution. On agitating, pure naphthalene picrate separates out, and is filtered. The precipitate is washed with N/40 picric acid solution to free it from acetic acid, and N/10 NaOH is added to it until there is an excess after boiling ten minutes. The reaction is $C_{10}H_8C_6H_2(NO_2)_3OH + NaOH = C_{10}H_8 + C_6H_2(N_2O)_3ONa$. The excess of soda is found by titration while hot, first, with N/20 picric acid and then with N to NaOH, using lacmoid indicator. From these data the amount of N/10 NaOH used up in the reaction is found; each cc. = 0·197 grains naphthalene.

The Re-precipitation Method.—The test is commenced in a similar manner to Colman and Smith's, only picric acid solution being used. The mixture of naphthalene and naphthalene picrate is filtered off and transferred to a flask, 50 to 100 cc. absolute alcohol being added. A clear yellow solution results. About 300 cc., concentrated picric acid solution are added, and on agitation pure naphthalene picrate separates out. The same procedure is subsequently followed as in the acetic acid method, only the washing with picric acid is omitted. Experiments proved both methods to be perfectly reliable and very rapid in execution.

A modification of this test is made use of in estimating naphthalene in spent oxide of iron. Ten grms. of the undried oxide are mixed with 100 cc. 80 per cent alcohol. The flask is agitated, allowed to stand several hours, and the liquid filtered. 300 cc. strong picric acid solution are added to the filtrate and washings. On agitation, naphthalene picrate separates out, and is treated as in the re-precipitation method.

"*Note on the Influence of Formal on the Properties of* Funtumia Elastica." By Dr. P. SCHIDROWITZ and F. KAYE.

The authors find that the rubber obtained from the latex treated by formal, although less elastic and resilient than that obtained by other means, was extraordinarily tough. They suggest that a rubber of this character might be particularly suitable for some purposes—*e.g.*, for the covers of motor tyres—where toughness is of relatively greater importance than resiliency, and that it may in the future be found desirable to use different methods of coagulation for the same latex according to the purpose for which the rubber is intended.

"*Polarimetric Determination of Sucrose.*" By FRANCIS WATTS and H. A. TEMPANY.

1. *Effect of Basic Lead Acetate on the Optical Activity of Sugar Solutions.*—In the polarimetric determination of sucrose in raw sugars the most suitable and convenient method of defecation is by means of basic lead acetate. Formerly solutions of the acetate were used, but it was shown that by this means errors of concentration were introduced owing to the space taken up by the precipitate formed. Horne proposed the use of the anhydrous acetate in place of a solution as almost removing this source of error, and the authors in a former paper supported this contention by further experimental work. But some investigators still maintain that there is a serious error in the polarimetric readings caused by the direct action of the basic acetate on the invert and non sugars present. In the present paper it is shown that in ordinary raw sugars if only slight excess of the basic acetate is used the error is so small as to be negligible. If large excess is used the error becomes serious. The error in reading is considered to be due to the basic portion of the lead present, and that if acetic acid is added sufficient to just neutralise the basicity the normal reading is restored. In the determination of molasses, however, the quantities of basic acetate required are so large that the error is considerable, and after partial clarification with anhydrous basic acetate the solution should be mixed with sulphur dioxide, which practically restores the normal rotation.

2. *The Effect of Clarification with Basic Lead Acetate on Cane-juice.*—In raw sugars clarified by basic acetate of lead the primary precipitates contain usually from 50 to 60 per cent of lead oxide, the basic acetate itself containing 81·4 per cent. The clarified liquor almost always contains lead, but still generally gives a further light lemon-yellow coloured precipitate on the addition of more basic acetate. The authors find this precipitate to contain 81 per cent of lead oxide and a very little organic matter which appears to be of a pectinous nature. They believe the lead present in the clarified juice to be due to traces of organic lead salts arising from the neutralisation of the basic lead by organic acids present in the sugars. The influence of these traces of lead salts in the clarified juices on the determination of invert by Fehling solution has been investigated, and it is found that this, though existent, is so slight as to be negligible unless large excess of basic oxide has been used.

"*Niam Fat.*" By Dr. J. LEWKOWITSCH.

Niam fat was obtained from the seeds of *Lophira alata* (Banks), a tree indigenous to Senegambia, Sierra Leone, and the Egyptian Soudan.

The fat freed from extraneous matter forms 41 per cent of the kernels. It is a soft buttery mass, melting at 24° C., and is used by the natives for culinary purposes and as a hair-oil.

The following characteristics were determined in two specimens :—

	Fat extracted from kernels.	Fat prepared by natives.
Sp. gr. at 40° C. (water at 40° = 1)	0·9105	0·9063
Acid value	18·54	5·78
Saponification value	195·6	190·1
Unsaponifiable matter	1·49	1·38
Iodine value	68·4	78·72
Mean molecular weight of the fatty acids	—	283·7
Solidifying point of the fatty acids	—	42·5° C.

Iodohydrines and Alkyliodohydrines derived from Styrolene.—Marc Tiffeneau.— When styrolene is subjected to the action of iodine in presence of yellow mercurous oxide in ethereal solution, the iodohydrine, $C_6H_5—CHOH—CH_2I$, is the only product, while in alcoholic solution the alkyliodohydrine $C_6H_5—CHOR—CH_2I$, where R varies according to the alcohol employed, is formed in addition. The oxy-alkyl group is always bound to the carbon atom next the aromatic radical, while the atom of iodine is attached to the carbon furthest from the C_6H_5 group, as may readily be proved in the case of the alkyl iodohydrines by transforming them into α-alkyloxy-styrolenes, $C_6H_5—CH(OR)—CH_2I \rightarrow C_6H_5C(OR)=CH_2$. The iodohydrine, $C_6H_5—CHOH—CH_2I$, is decomposed as follows by distillation *in vacuo* :—

$$C_6H_5—CH(OH)—CH_2I \rightarrow C_6H_5C(OH)=CH_2 \rightarrow \rightarrow C_6H_5—CO—CH_3,$$

the final product being acetophenone and not phenyl acetic aldehyde. Alcoholic potash transforms this iodohydrine into mono-ethers of phenyl glycol, which are decomposed by sulphuric acid into phenyl acetic aldehyde and not into acetophenone.—*Comptes Rendus*, cxlv., 20.

NOTICES OF BOOKS.

Practical Chemistry. By GEOFFREY MARTIN, B.Sc., Ph.D. London: Crosby Lockwood and Son. 1907.

THIS short course of practical chemistry for army and matriculation candidates, and for use in secondary schools, includes both qualitative and quantitative work. Full directions are given for the preparation of typical gases and salts. The apparatus described is in most cases relatively simple, and the experiments are well chosen for illustrating important reactions and operations. In a book of this type it is difficult to avoid a certain resemblance to a collection of recipes, especially when the author is aiming at sparing the teacher's tutorial work as far as possible; but, on the whole, the student is induced to think for himself, and the exercises and problems upon the work he has done should encourage him to devise simple experiments. The quantitative work includes gravimetric estimations, volumetric analysis, and the determination of solubility, boiling- and melting-points. A chapter on the regulation of work in practical chemistry classes will be appreciated by teachers who find it difficult to estimate and register the progress of their students, and the adoption of the author's suggestions would seem likely to promote a healthy spirit of rivalry in the workers, and to put before them a high ideal of carefulness and accuracy.

The Metric and British Systems of Weights, Measures, and Coinage. By F. MOLLWO PERKIN, Ph.D. London and New York: Whittaker and Co. 1907.

ALTHOUGH the author of this book had more particularly the requirements of science students in his mind when he wrote it, the introduction is addressed more to the great majority of the public who are still unconvinced of the advantages which will follow the universal adoption of the metric system. Dr. Perkin puts his case very clearly and strongly, and gives useful comparisons of well known quantities, which are readily remembered in the metric system, such as the thickness of a sixpence, the width of a stamp, and so on, which will help the student to form a mental picture of the relative magnitude of the English and metric units. For rough calculations the graphs will be found invaluable. There are some worked examples in the book, and the use of the balance and the determination of specific gravity are also described. It seems a pity that the fundamental difference between density and specific gravity is not emphasised for the benefit of the student, even if for general purposes it is thought that such distinctions are unnecessary, and a slip in speaking of a cube of aluminium in centimetres and the weight of a centimetre of water will possibly cause some confusion in the beginner's mind.

Liquid and Gaseous Fuels. By VIVIAN B. LEWES, F.I.C., F.C.S., &c. London: Archibald Constable and Co., Ltd. 1907.

THE author of this book thoroughly understands how to interest the lay reader, and gives a very practical account of the use of liquid and gaseous fuels in power production. The subject is one which in some aspect or other is of considerable moment to a vast section of the general public, and some parts of the book, such as, for instance, those which treat of the calorific value of coal-gas and the heating and illuminating power of oil-lamps, will perhaps help the consumer to form an estimate of the cost and efficiency of various systems of heating and cooking under different conditions. The evolution of the common forms of gas-burners is discussed in some detail, but perhaps the most interesting section of the book is that in which the author forecasts the probable future of the fuel question. He suggests that the peat deposits of the world will shortly be utilised to a much greater extent than they are at present, and believes that when they are exhausted, or even before then, the production of alcohol by fermentation will provide the solution of the problem of the fixation of solar energy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 20, November 11, 1907.

Iodation in Vacuo.—Marcel Guichard.—Ferrous iodide can be prepared by placing iodine and iron separately in a sealed tube which is exhausted by a mercury pump. The part of the tube containing the iron is heated to 500°, and that containing the iodine to 180°. The iodine then vaporises and unites with the iron. Ferrous iodide is dark red in colour. By the same method anhydrous nickel iodide and uranium iodide can also be prepared. In order to prepare iodides which are formed at a high temperature and are very volatile—for example, silicon or aluminium iodide—it is necessary to keep the sealed tube at three different temperatures. All these iodides are formed at pressures lower than atmospheric.

Action of Amorphous Arsenic upon Alkyl Haloids.—V. Auger.—Amorphous arsenic precipitated from a hydrochloric acid solution of arsenious anhydride by stannous chloride or by hypophosphite, is capable of inducing many chemical reactions. Thus, when it is heated in a sealed tube with carbon tetrachloride the hexachloride is formed, $6CCl_4 + 2As = 2AsCl_3 + 3C_2Cl_6$. With chloroform amorphous carbon is formed: $3CHCl_3 + 2As = 2AsCl_3 + 3HCl + 3C$. Iodoform and amorphous arsenic react with an explosion when heated together on the water-bath. If a neutral solvent, such as benzene or toluene, is employed the action proceeds quietly, and the study of the reaction shows that it occurs quantitatively according to the equation $3CHI_3 + 2As = (CHI_2)AsI_2 + (CHI_2)_2AsI$. Nitric acid with these iodides gives the corresponding acids:—

$$(CHI_2)AsI_2 + 4HNO_3 = (CHI_2)As{<}^{O}_{OH} + 4NO_2 + H_2O \text{ and}$$

$$(CHI_2)_2AsI + 3HNO_3 = (CHI_2)_2As{=}O{<}_{OH} + 3NO_2 + H_2O.$$ Di-iodomethyl arsenic acid crystallises in yellow tablets with one molecule of water. Warm aqueous solutions of alkalis decompose it quantitatively as follows:—$(CHI_2)AsO_3H_2 + 2NaOH = CH_2I_2 + AsO_4HNa_2 + H_2O$. Tetra-iodo cacodylic acid with soda gives methylene iodide and arsenate.

Action of Urea, Thiourea, and Urethane, and some Amides on Xanthone Hydrol.—R. Fosse.—With a certain number of primary amides xanthone hydrol gives one molecule of water and a monamido monoxanthane compound. With unsubstituted diamides, such as urea or thiourea, the reaction is similar, one molecule of the diamine combining with two of the xanthone hydrol,—

$$O{<}^{C_6H_4}_{C_6H_4}{>}CHOH + O{<}^{C_6H_4}_{C_6H_4}{>}CHOH + {}^{HNH}_{HNH}{>}CO =$$

$$= H_2O + \left[O{<}^{C_6H_4}_{C_6H_4}{>}CH\right]^{NH}_{NH}CO.$$

One molecule of xanthone hydrol reacts with sulpho-urea, giving phenyl monoxanthyl sulpho-ureas. The xanthones monamides and dixanthone diamides react with acids as follows :—

$$\left[O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\right][NH.CO.R] + HCl =$$

$$= NH_2COR + CH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>OCl.$$

$$\left[O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\right]NH\\ \left[O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\right]NH\Big\rangle CO + 2HCl =$$

$$\begin{matrix}NH_2\\NH_2\end{matrix}\Big\rangle CO + 2CH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>OCl.$$

Application of Hofmann's Reaction to Sparteïne.—Charles Moureu and Amand Valeur.—The products obtained by applying Hofmann's reaction to the hydrate of α-methyl sparteïne are :—Methyl sparteïne, $C_{15}H_{25}N_2CH_3$; dimethyl sparteïne, $C_{15}H_{24}N_2(CH_3)_2$; and, finally, hemisparteïlene, $C_{15}H_{23}N$. These all behave like mixtures, and the authors have not attempted to extract definite products from them. Raw methyl sparteïne, when subjected to the action of methyl iodide, is only 66 per cent methylated, and when the non-methylated part is separated off a raw dimethyl sparteïn is obtained. With excess of methyl iodide this gives di-iodomethylate, converted by silver oxide into the dihydrate of tetramethyl sparteïne, the decomposition of which gives methyl hemisparteïlene, $C_{16}H_{25}N$.

Determination of Fat in Skim Milk.—R. Lezé.—The fat remaining in skim milk can be very rapidly determined as follows :—A solution of caustic soda, 20 grms. in 150 to 180 cc. of ammonia, is made up to 250 cc. To 3 litres of the milk heated to 40°, 6c cc. of this reagent are added, and the milk is then skimmed again in a separator. It is found that all the fat is concentrated in the cream, which can then be analysed by any of the usual methods.

MISCELLANEOUS.

Royal Institution.—*Friday Evening Meetings before Easter*, 1908 :—

January 17, Prof. T. E. Thorpe, C.B., Ph.D., LL.D., D.Sc., F.R.S., M.R.I., "The Centenary of Davy's Discovery of the Metals of the Alkalis."
January 24, Colonel David Bruce, R.A.M.C., C.B., D.Sc., F.R.S., "The Extinction of Malta Fever."
January 31, Prof. Ernest Rutherford, M.A., LL.D., D.Sc., F.R.S., "Recent Researches on Radio-activity."
February 7, Humphry Ward, Esq., M.A., "Napoleon and the Louvre."
February 14, Caleb Williams Saleeby, Esq., M.D., F.R.S.E., "Biology and History."
February 21, Sir Oliver Lodge, LL.D., D.Sc., F.R.S., M.R.I., "The Ether of Space."
February 28, Prof. William Arthur Bone, D.Sc., Ph.D., F.R.S., "Explosive Combustion, with Special Reference to that of Hydrocarbons."
March 6, Prof. John Milne, D.C.L., D.Sc., F.R.S., F.G.S., "Recent Earthquakes."
March 13 (Vacant).
March 20, Prof. A. E. H. Love, M.A., D.Sc., F.R.S., "The Figure and Constitution of the Earth."
March 27, Hon. Robert John Strutt, M.A., F.R.S., "Radio-active Change in the Earth."
April 3, The Rt. Hon. Lord Montagu of Beaulieu, D.L., V.D., J.P., &c., Vice-Ptesident, Royal Automobile Club, Editor of the *Car*, "The Modern Motor-car."
April 10, Prof. Joseph Thomson, M.A., LL.D., D.Sc., F.R.S., M.R.I., "The Carriers of Positive Electricity."

MEETINGS FOR THE WEEK.

MONDAY, 16th.—Society of Arts, 8. (Cantor Lectures). "Theory of the Microscope," by Conrad Beck, F.R.M.S.
TUESDAY, 17th.—Society of Arts, 8. "How to Make the Most of a Museum," by Lewis Foreman Day.
WEDNESDAY, 18th.—Microscopical, 8. "Some African Rotifers," by J. Murray. "Gregory and Wright's Microscope" and "A Correction for a Spectroscope," by E. M. Nelson. Exhibition of Selenite Specimens, showing interesting Features due to Twinning, by E. Large.
—— Society of Arts, 8. "The *rôle* of France in West Africa," by Mons. Lucien Hubert, Député des Ardennes. (The author will read his paper in French).
THURSDAY, 19th.—Chemical, 8.30. "Derivatives of Tetramethyl Glucose," by J. C. Irvine and A. M. Moodie. "Characterisation of Mercerised Cotton," by J. Hübner. "Attempted Synthesis of $\begin{matrix}\beta\text{—}N\text{—}\beta\\ |\\ \beta\text{—}CH\text{—}\beta\end{matrix}$ dinaphthacridine—Condensation of Methylene Dichloride and 1-Substituted-2-naphthylamines," by A. Senier and P. C. Austin.

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Clerk to the Governing Body.

THE CHEMICAL NEWS.

Vol. XCVI., No. 2508.

THE ORIGIN OF COLOUR IN ORGANIC COMPOUNDS.

By PERCY MAY.

(Concluded from p. 285).

Part II.

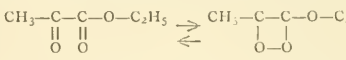
So long as attention was paid only to whether a substance was coloured or not, little progress could be made as the subject was necessarily of a qualitative and empirical nature. The application of spectroscopy has brought a new and searching light to bear upon the problem of colour, and has furnished the quantitative basis necessary to raise the study of the origin of colour to the level of an exact science.

Hartley was the chief pioneer in the study of the ultra-violet absorption spectra of organic compounds, and he has discovered certain most important facts connecting chemical constitution and absorption spectra. The method employed by Hartley was to measure the absorption limits at a great many concentrations, always gradually increasing the dilution until complete transmission was obtained. The oscillation frequencies of the edges of the regions of absorption were then plotted against the corresponding strengths of solution, and a curve drawn through the points so obtained. It is the shape of these curves that has been connected with the chemical constitution of the substances.

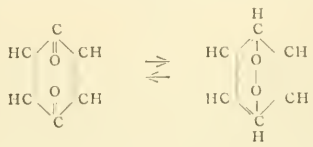
Recently much work has been done in this direction by Baly and others, and they have employed a slightly different form of plotting the results. Hartley, in his later work, plots equivalent thickness of solution instead of strength of solution, while Baly and his co-workers have plotted the logarithms of the relative thickness instead of the values themselves. This method has the great advantage that a given relative change of concentration is represented by the same change of ordinates in any part of the diagram. In his investigation of the spectrum of benzene, Hartley discovered six absorption bands close together, but later Baly and Collie found seven (*Trans. Chem. Soc.*, 1905, lxxxvii., 1332). Now, in the vibration of the benzene molecule, as described by Collie (*Trans. Chem. Soc.*, 1897, lxxi., 1013), there are seven possible changes of linkage between the carbon atoms, and therefore it seemed highly probable that the actual linkage change is the cause of the absorption band. This, for the first time, actually indicates a physical cause of colour, and subsequently Baly and Desch, from their investigation of acetyl acetone, $CH_3.CO.CH_2.CO.CH_3$, obtained results in accordance with this view. They found that the absorption was the same if the hydrogen were replaced by beryllium, sodium, or even the very heavy thorium. They therefore concluded that the absorption was not due to the vibration of the atom itself (H, Be, Na, or Th) but to the actual change of linkage, $CH_2—CO— \rightleftarrows —CH=COH$, in the molecule brought about by enol-keto tautomerism, $CH_3.CO.CH_2.CO.CH_3 \rightleftarrows CH_3—CO.CH=C(OH)—CH_3$, and this was confirmed by the fact that neither the pure ketonic nor the pure enolic form of aliphatic tautomeric substances gave an absorption band.

Subsequently, Baly and Stewart investigated the spectra of substances containing the carbonyl group, such as ketones and quinones, and from the results obtained they concluded that the reactivity of any carbonyl group is not inherent in the group itself, but is produced by the reaction of neighbouring atoms. It is supposed that such action may take the form of tautomerism, or of a modification of tautomerism, in which there is no actual transfer of a hydrogen atom, but some inter-atomic disturbance in the grouping $—CH_2—CO—$.

It was found from a study of substances containing two carbonyl groups in the α-position to one another, that in those cases the position of the absorption band was shifted towards the red, with the production therefore of colour. As an example, pyruvic ester has an absorption band of great persistence at a frequency of 2070. In this case, the inter-atomic isturbance can be represented, as—



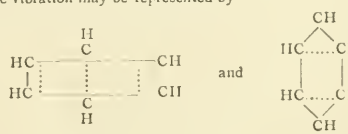
and Baly and Stewart propose the term isorropesis to denote this finer play of forces between two carbonyl groups. The theory of isorropesis will give an explanation of the cause of colour in quinonoid bodies, for isorropesis can occur between the residual affinities of the oxygen atoms, which results in the absorption of light in the visible region of the spectrum. It has not been possible to



give more than a sketch of the theory of isorropesis, but a clear account of it is given by Baly and Stewart in the *Astrophysical Journal*, Sept., 1906, xxiv., p. 100, and in the *Transactions of the Chemical Society*. These results are not antagonistic to the ordinary theory of quinonoid structure, but, on the contrary, they supply the key to it, and indicate *why* quinonoid bodies should be coloured.

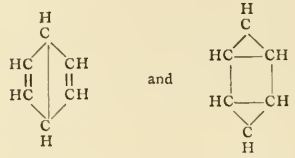
In considering the colour of diphenylfulvene and of diphenylquinomethane, attention was drawn to the fact that the colour was more pronounced in the case of a molecule containing ethylenic double bonds than in one in which these double bonds have been replaced by an aromatic ring. In the former case there is, according to modern views, a far greater residual affinity, and it is the presence of this residual affinity that causes inter-atomic disturbances and isorropesis, and therefore colour.

It has been previously stated that the ordinary theories do not offer any explanation of the colour of compounds, such as meta-nitraniline, but by a consideration of the modern views of the constitution of benzene, Baly, Edwards, and Stewart have ingeniously extended the theory of isorropesis to include meta-quinones. They found that the three nitranilines and the three nitrophenols in alkaline solution give absorption spectra which indicate the existence of a quinonoid form, and the process of isorropesis as the origin of colour. It is therefore necessary to assume the transitory existence of a meta-quinone, and this is possible if the benzene molecule be regarded as undergoing the same vibrations as are suffered by an elastic ring. This vibration theory of the benzene molecule accounts for many of the physical properties of the substance and is widely accepted. The extreme phases of the vibration may be represented by—



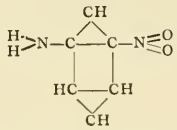
(*a*). (*b*).

or using the ordinary hexagon formula, these same two extreme phases between which the molecule is pulsating are :—

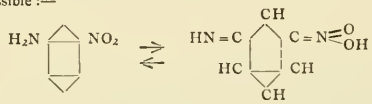


(*a'*). and (*b'*).

The ordinary formula for meta-nitraniline in phase (*b*) is—

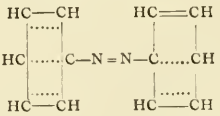


but in this phase isorropesis involving a meta-quinone is possible :—

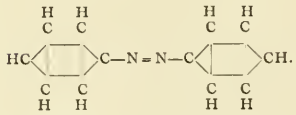


This conception of the meta-quinone is, of course, of very great value, as it can be applied to many compounds of which the colour cannot be explained by the older theories.

The elastic ring theory of benzene is also made use of by Baly and Tuck to account for the colour of the azo-compounds. Thus azo-benzene, $C_6H_5—N=N—C_6H_5$, will exist in the extreme phases—

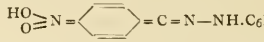


and—

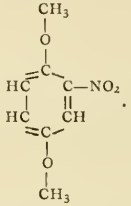


In the second phase, the C atoms, which are united to the N, are unsaturated, and therefore isorropesis can occur between them and the N atoms. This view is in harmony with the fact that $C_6H_5—N=N—CH_3$ is far less coloured than $C_6H_5—N=N—C_6H_5$, and similarly when the C_6H_5 is replaced by any alkyl group. When exposed to light the hydrazones of the aldehydes become yellow, and Baly and Tuck (*Trans. Chem. Soc.*, 1906, lxxxix., 983) have obtained very complete evidence to show that the compound so formed is an azo-compound, the colour of which is, of course, explainable on the above hypothesis.

The actual hydrazones of the nitrobenzaldehydes are brilliant yellow, and in this case the spectra are quite similar to those of the nitrophenols and totally different from those of the azo-compounds, and it therefore appears that they, like the nitrophenols, exist in the quinonoid form :—



Until very recently, the theory of isorropesis was able to account for practically every case of colour due to the linkage of the atoms, but, now some facts have been brought to light which cannot be explained by its aid, and necessitate a new development of the subject. Thus, nitrodimethylquinol,—



is said to be bright yellow, and its colour cannot be accounted for by any existing theory. Much therefore still remains to be done, but there can be no doubt that spectroscopic methods have thrown much light on chemical constitution where purely chemical methods have failed. Certainly, a study of colour theories, past and present, will convince one of the truth of Hartley's statement, that "by the systematic study of absorption spectra can we alone obtain the necessary accumulation of facts which may enable us to arrive at a just conclusion as to the origin of colour."

THE

EFFECT OF HEATING YELLOW PHOSPHORUS IN AMMONIA GAS.

By WILLIAM G. LLEWELLYN.

ALTHOUGH the action of ammonia on compounds of phosphorus is well known, the action of the gas on the element (yellow and red) does not appear to have attracted much attention.

It was thought that excess of ammonia might give either the amines $P(NH_2)_3$ and $P(NH_2)_5$, and phosphine, or perhaps the nitride P_3N_2, and phosphine.

The result of an investigation of the point shows that between the temperature 10° C. and 290° C. (*i.e.*, the boiling-point of phosphorus) there is no action. The results are, however, interesting.

A Würtz flask fitted with an inlet tube reaching nearly to the bottom of it. A thin small flask fitted to the stem acted as receiver, and was cooled by a current of cold water. The outlet tube from the receiver was placed in one of the holes at the bottom of a Bunsen burner, that any phosphine from reactions might be decomposed and the excess of ammonia gas also destroyed. The ammonia was prepared from the aqueous solution by warming, and dried by passing up one tower of quick-lime. The flask was also fitted with a T-tube so that the current of gas could be easily stopped if necessary.

Ammonia was passed through the apparatus for fifteen minutes to expel all the air. A piece of phosphorus, freshly cut so as to expose a clean surface, and dried, was then introduced into the flask. Ammonia gas was passing all the time. No action resulted even on gently heating the flask until the phosphorus melted. On heating the phosphorus to its boiling-point it was found that a white substance condensed on the cooler parts of the flask, and

afterwards clear colourless globules also condensed in the stem. By warming this part of the apparatus the substance was partly driven over into the receiver. During this time the end of the exit tube was dipping into ammoniacal copper sulphate solution, but no copper phosphide was formed, therefore no phosphine had been produced. The whole of the phosphorus had been distilled, none remaining in the Würtz flask. The apparatus was cooled and the distillate examined.

On admitting air to the small flask the white substance was found to glow, and gave off white fumes, indicating unchanged phosphorus. The clear colourless globules in the stem of the flask were examined and found to be solid. The melting-point corresponded with that of ordinary phosphorus. On standing in air so that superficial oxidation might begin, the phosphorus became yellow, like ordinary yellow phosphorus. On warming with water it gradually returns to the ordinary modification. It was found to be soluble in carbon bisulphide.

Remsen and Keiser (CHEMICAL NEWS, xlviii., 201) obtained white phosphorus by distilling yellow phosphorus in a current of purified hydrogen. The method now described is probably simpler and is not dangerous, as no free hydrogen is present to cause the explosive mixture which they state is liable to be obtained in the final operation of their method. No special purification of the ammonia gas is necessary either.

Ammonia gas passed over red phosphorus between 10° C. and 100° C. has no apparent action, the phosphorus remaining unchanged.

Conclusion.—White phosphorus may be obtained by distilling yellow phosphorus in a current of ammonia gas.

The Polytechnic, Regent Street, London.

A METHOD FOR THE DETECTION OF COCOANUT OIL IN BUTTER FAT.

By T. R. HODGSON, B.A., A.I.C.

THIS research was not undertaken with a view to increasing the already voluminous literature on this subject, but with a view to obtaining some method which is short and easily workable in a practical laboratory, and which at the same time enables the sophistication of butter fat with cocoanut-oil to be detected with certainty.

The author has shown (CHEMICAL NEWS, 1907, xcv., 121) that the methods at present in use for the detection and estimation of cocoanut oil in butter fat are more or less useless.

At the present time butter may be unblushingly placed on the market which is known to be adulterated with this oil, and, owing to the present state of the law, it is almost impossible to detect this fraud, for the adulteration is carried on so scientifically that the constants of the mixture are kept within the range of the constants which are usually taken to be consistent with pure butter.

The method followed in this paper is that described in the two previous papers for the determination of the "oxygen equivalent," but it would perhaps be as well to give the method again.

One grm. of the filtered fat is weighed out into a flask, and 25 cc. of a half normal alcoholic solution of caustic potash are added; the flask is then attached to a reflux condenser, and the whole is heated on a boiling water-bath for thirty minutes.

After the saponification is complete, the flask is detached from the condenser, and the solution is evaporated to dryness on the water-bath; 50 cc. of distilled water are then added, and the whole evaporated again to dryness; this operation is continued until the whole of the alcohol has been driven off.

After the whole of the alcohol has been driven off, the residue is dissolved in water and made up to 1000 cc.; 20 cc. of this solution are measured out into a beaker, and 50 cc. of a tenth-normal solution of potassium permanganate, and 50 cc. of a roughly 50 per cent solution of sulphuric acid are added; the beaker is then placed on a boiling water-bath for half-an-hour, and the excess of potassium permanganate titrated with a standard solution of ferrous ammonium sulphate.

The number of cc. of potassium permanganate solution used multiplied by 4 gives the "oxygen equivalent" or the number of grms. of oxygen required to oxidise 100 grms. of the oil or fat. The numbers obtained with mixture of butter fat and cocoanut oil were as follows:—

Sample.	Cc. of $K_2Mn_2O_8$ used.	Difference.
A.	41·8	
B.	40·2	1·6
C.	38·0	2·2
D.	35·6	2·4
E.	34·0	1·6
F.	31·8	2·2
G.	29·6	2·2
H.	27·6	2·0
M.	25·8	1·8
P.	23·8	2·0
Q.	21·8	2·0

Even a cursory glance at the numbers given above will show that the difference, though not quite so, is very nearly constant; the average difference between any two samples is 2·0, and it will be seen that no two samples differ more than 0·4 of a cc. from the average.

Sample.	"Oxygen equivalent."	Cocoanut oil (per cent.)	
		Calculated.	Actual.
A.	167·2	—	—
B.	160·8	8	10
C.	152·0	19	20
D.	142·4	31	30
E.	136·0	39	40
F.	127·2	50	50
G.	118·4	59·7	60
H.	110·4	71·0	70
M.	103·2	80	80
P.	95·2	90	90
Q.	87·2	—	100

The Sample A was pure butter fat and the Sample Q pure cocoanut oil.

In three cases the calculated percentage of cocoanut oil agrees exactly with the actual percentage, in two cases the calculated percentage is in excess of the actual, and in the other four cases the calculated percentage is slightly less than the actual.

The author hopes that the method described in this and the two preceding papers will be found to be of use in the detection of this the most disgraceful form of adulteration, or that it may form a foundation on which may be built in the future a superstructure sufficiently strong to obtain the desired object.

Analytical Department,
University of Birmingham.

Lupeol.—P. van Romburgh.—When lupeol is boiled with acetic anhydride in presence of sodium acetate a product is obtained which boils at 212—213°, and which causes a considerable lowering of the melting-point of lupeol. Its analysis shows that it is an acetate. When lupeol is obtained from "bresk" it behaves quite differently under the action of these reagents, which led the author to investigate the effect of heat upon it. When it is heated in a glass boat in an exhausted tube furnished with a reservoir containing sulphuric acid a sublimate is found in the tube. There is no loss of water on heating to 190°, and hence it must be concluded that the substance is converted into another modification.—*Comptes Rendus*, cxlv., No. 22.

THE NITROSO-β-NAPHTHOL METHOD FOR THE QUALITATIVE SEPARATION OF NICKEL AND COBALT.

By WILLIAM H. CHAPIN.

THE nitroso-β-naphthol method for the qualitative separation of nickel and cobalt is not a new one; and, in view of what has already been written on the subject, anything further may seem superfluous. However, this paper has two excuses to offer for its existence.

1. For the sake of those who are unacquainted with the method, it will aim to make the directions for the cobalt test more explicit than those usually given.

2. It will present a method for determination of the nickel, which so far as the author knows is new.

The things this paper contains may be familiar to many; but for the sake of benefitting those who are still wandering in the dark, I shall brave the fear of repetition, and give them out for what they are worth.

COBALT.

Beginning at the point where the nickel and cobalt exist alone as sulphides after removal of zinc and manganese, we proceed as follows:—

Place paper and contents in a casserole, add 10 cc. dilute hydrochloric acid (1 : 4) and 1 cc. dilute nitric acid (1 : 3) and boil until only the paper and separated sulphur remain undissolved. Now filter, washing the paper slightly, return the filtrate to the casserole, and boil down to complete dryness, taking care to remove the casserole from the flame a little before this point is reached, so as not to overheat and render the residue insoluble. Take up with two or three drops of dilute hydrochloric acid and 10 cc. hot water, and add a solution of nitroso-β-naphthol in slight excess. The cobalt comes down as a very bulky brick-red precipitate of cobalti-nitroso-β-naphthol, $Co(C_{10}H_6ONO)_3$. After stirring and allowing to stand a few minutes, filter, and confirm the presence of cobalt by means of the borax bead. Before testing for nickel, add a few drops more nitroso-β-naphthol to the filtrate to make sure that the cobalt is all removed, and of course filter off any precipitate that may be formed.

Notes.

Hydrochloric acid in large quantities and nitric acid even in small quantities interfere with the precipitation of cobalt; hence the evaporation.

The solution of nitroso-β-naphthol is made up as follows:—Weigh out 8 grms. of the solid reagent, dissolve in 300 cc. cold glacial acetic acid, dilute with an equal volume of water, and filter. In this way is obtained a saturated solution in 50 per cent acetic acid. For best results, the reagent should be made up as often as once a month, as it does not keep very well.

Owing to the bulkiness of the cobalt precipitate, we usually make up our unknowns with only a small amount of cobalt present (2 grms. crystallised cobalt nitrate per litre). Giving out about 5 cc. of such a solution in an unknown, only about 3 cc. nitroso-β-naphthol solution will be required for complete precipitation. It is, however, by no means necessary to limit the quantity of the cobalt.

The test for cobalt, as above stated, has always given perfectly satisfactory results even with beginners, good tests for cobalt being obtained with certainty, when the quantity present was less than a milligrm. Indeed, we have had difficulty in obtaining nickel salts of such purity that our students would not obtain a test for cobalt even when we did not intend it to be present.

NICKEL.

The main difficulty we have experienced with the method has rested with the test for nickel. In their usual form the directions for this test read as follows:—"Make the filtrate from cobalt alkaline with ammonium hydroxide, filter off the precipitated nitroso-β-naphthol, and pass hydrogen sulphide. Confirm the presence of nickel by means of the borax bead."

So far as our experience goes, the test in this form has always been a failure. With our classes failure became so common that the students lost all confidence in the method, and reported largely at random. We even made up our unknowns so that the amount of nickel exceeded that of cobalt ten to one (which only showed the weakness of the method and in no wise overcame it), and even then the number of failures was scarcely less. However, considering the shortness and simplicity of the method and its accuracy for the detection of cobalt, we determined not to give it up without some attempt at making it what it promised to be.

Thinking that possibly the nickel might be lost during the washing of the sulphides, as a result of oxidation and consequent solution, we investigated and found that the loss of nickel from this cause was not worse than the loss of cobalt, which amounted to very little.

Next, we tested the solubility of nickel sulphide in the cold dilute (1 : 10) hydrochloric acid used to dissolve out zinc and manganese, but here again the loss was found to be very small.

At last we turned our attention to the final filtrate in which hydrogen sulphide had failed to give a precipitate of nickel sulphide when nickel salts were known to be present in the original solution. We thought that perhaps the organic matter left in the solution was preventing the precipitation, but were surprised to find that this filtrate contained no nickel. The cause of the difficulty was now plain: In making the solution alkaline, and filtering off the precipitate of nitroso-β-naphthol, we were removing from the solution large quantities of nickel, the amount removed depending upon the excess of nitroso β-naphthol.

What we needed, then, was a method by which we could remove the nitroso β-naphthol, so that the solution might be made alkaline for precipitation of nickel without removing the nickel. The method most easily worked out seemed to be the common one for removal of organic matter, viz., oxidation by means of sulphuric and nitric acids. Trial proved the method to be quick, easy, and always successful. Best of all, it did not interfere in any way with the subsequent test for nickel.

The details of this process as we apply it and of the final test for nickel are as follows:—

To the filtrate from cobalt add 5 cc. of dilute sulphuric acid (1 : 5) and 1 cc. of nitric acid (1 : 3), and boil down in a casserole until dense white fumes of sulphur trioxide are evolved. If a dark colour still remains, cool somewhat, add two or three drops more of nitric acid, and again heat until fumes of sulphur trioxide appear. By this time all organic matter should be removed and the solution should be coloured only yellow at most. Cool now completely, cautiously add 5 cc. water and a piece of litmus-paper, and then drop in ammonium hydroxide with constant stirring until the paper is distinctly blue, but avoiding an excess. Now remove the paper, transfer the solution to a test-tube, and pass hydrogen sulphide. A black precipitate is probably nickel. Confirm by means of the borax bead.

Note.

If through careless work the cobalt is not all removed in its proper place, the excess will appear with the nickel; or, if no nickel is present, in place of the nickel. However, we have never seen enough cobalt carried over to obscure the bead test for nickel, where that element was present; and, on the other hand, in absence of nickel, the bead test never fails to disclose the identity of the small amount of cobalt sometimes carried over. If the work is carefully done, no cobalt will ever be carried over, as its removal by this process is quantitative.

We have been using this method for the nickel determination long enough to discover the weak points, if there

were any, and are perfectly satisfied with the results. Failure on the part of our students is a very rare thing, although we have greatly cut down the amount of nickel in our unknowns. I think we are safe in saying that the test for nickel is fully as delicate as that for cobalt; and the ease and rapidity with which it is carried out make it the best method, in our estimation, we have ever used.—*Journal of the American Chemical Society*, xxix., No. 7.

THE DETERMINATION OF CHLORIDES OR BROMIDES IN THE PRESENCE OF SULPHOCYANATES.*

By M. A. ROSANOFF and ARTHUR E. HILL.

1. *Introductory*

In the course of a research undertaken in the Havemeyer Chemical Laboratory, New York University, it became necessary to analyse a number of solutions containing mixtures of chlorides and sulphocyanates. Investigation of the literature of the subject showed that no method exists by which such mixtures can be analysed quickly and accurately; it was found that those methods which can be relied upon for accuracy of results require such expenditure of time as prohibits their use where large numbers of analyses must be performed. In like manner search revealed no suitable method for the analysis of bromide-sulphocyanate mixtures.

To remedy this lack, the following volumetric method is proposed. It permits of an accuracy within the limits of the usual errors of measurement with pipettes and burettes, and requires less time than any of the existing methods; a single complete determination has been found to require about one and one-half hours, while two determinations can be performed without difficulty in two hours. By proper organisation of the work eight to ten analyses can easily be made within a working day.

The sum of chloride and sulphocyanate, or of bromide and sulphocyanate, is established by precipitation with excess of standardised silver nitrate and determination of the excess by titration with standardised ammonium sulphocyanate, according to the method of Volhard (*Journ. Prakt. Chem.*, 1874, ix., 217; *Zeit. Anal. Chem.*, 1874, xiii., 171). Precipitates containing silver chloride must be filtered off before the excess of silver nitrate is determined, while in the case of the bromide filtration is unnecessary (Rosanoff and Hill, *Journ. Am. Chem. Soc.*, 1907, xxix., 269; Chemical News, xcvi., 264; *Chem. Centr.*, 1907, i., 1596). The new method has for its object the determination of the chloride or bromide in a fresh sample of the solution, by oxidising the sulphocyanate to hydrocyanic acid by means of nitric acid, expelling nearly all the hydrocyanic acid, and determining the residual chloride or bromide, in the presence of the traces of cyanide, by the Volhard method. The sulphocyanate originally present is found by difference.

2. *Determination of Chlorides.*

The following solutions are required:—(*a*) A fifteenth-normal solution of silver nitrate, standardised gravimetrically or by weight of silver nitrate used; (*b*) a fifteenth-normal solution of ammonium sulphocyanate, standardised against the silver nitrate by Volhard's method; (*c*) a saturated solution of iron-ammonium alum, free from chlorides, and treated with nitric acid to lighten the colour.

A measured volume of the chloride-sulphocyanate mixture is diluted so that the normality of the chloride is about one-fiftieth. The solution is treated with 1 cc. of the iron-ammonium alum, and brought to a boil in a large Erlenmeyer flask. To the gently boiling solution concentrated nitric acid is added at the rate of about three drops a minute, during which operation the liquid should be frequently stirred to prevent superebullition. The addition of the acid in the above described manner is continued until the colour of the solution has faded to a *pale orange*, and then without further addition of acid the solution is allowed to boil for a few minutes longer, by which treatment the last traces of sulphocyanate are oxidised. The complete oxidation requires about twenty minutes time; a change of colour to pure yellow indicates the completion of the operation. The odour of hydrocyanic acid is now practically gone.

Cool the solution thoroughly under the tap, and add to it one-third its volume of concentrated nitric acid. Add a measured amount of N/15 silver nitrate in moderate excess above the quantity required to precipitate the chloride, and shake the mixture until the precipitate is well coagulated, which requires but a few minutes' agitation when the solution is cool, but *a much longer time if the solution is heated*. When the precipitate is well coagulated bring the solution again to a gentle boil, maintaining it at this temperature for about five minutes. The liquid above the precipitate must become perfectly clear.

Filter the solution while still hot through a rapid-running double filter, paying no attention to the opalescence which forms in the filtrate upon cooling. Wash the precipitate with hot water containing a few drops of nitric acid. Allow the liquid to cool thoroughly, dilute until the volume is about three times that of the solution before filtration, add 2 cc. of the iron indicator for every 100 cc. of solution, and run in the standardised sulphocyanate to a strong red colour. Stir the solution for five minutes, and then add the standardised silver nitrate drop by drop, with stirring, until the colour just disappears. A single drop of the sulphocyanate solution should then give a permanent pink colour; should it fail to do so, titrate back and forth with the silver nitrate and ammonium sulphocyanate until the colour changes on addition of a single drop. The titration is best conducted in a porcelain dish, against the white ground of which the end-point is most accurately determined; in glassware transmitted light effects may be misleading. The total silver nitrate added, *minus* the total ammonium sulphocyanate added, is the silver nitrate equivalent of the chloride present.

The following is a list of ten consecutive analyses of mixtures of potassium chloride and sulphocyanate performed according to the foregoing directions:—

	N/15 KCl solution. Cc.	N/15 KCNS solution. Cc.	$AgNO_3$ equivalent of KCl taken.	$AgNO_3$ equivalent found.	Absolute error. Cc.
1.	0·00	25·00	0·00	0·02	+0·02
2.	10·00	90·00	9·95	9·96	+0·01
3.	25·00	50·00	24·87	24·87	0·00
4.	25·00	50·00	24·87	24·86	−0·01
5.	25·00	25·00	24·87	24·88	+0·01
6.	25·00	25·00	24·87	24·93	+0·06
7.	25·00	10·00	24·87	24·83	−0·04
8.	25·00	5·00	24·87	24·90	+0·03
9.	25·00	3·00	24·87	24·84	−0·03
10.	25·00	0·15	24·87	24·90	+0·03

3. *Determination of Bromides.*

The analysis of bromide-sulphocyanate mixtures is conducted precisely as that of the chloride mixtures, with three modifications:—(*a*) the solution to be treated with nitric acid for the destruction of the sulphocyanates should be diluted to roughly one-hundredth normality with respect to bromides; (*b*) after the sulphocyanate has been decomposed at the boiling temperature and the liquid thoroughly cooled, only one-sixth its volume of concentrated nitric acid is added; (*c*) the precipitated silver salts should not be filtered off before the excess silver nitrate is determined.

* Presented before the New York Section of the American Chemical Society, May 10, 1907. From the *Journal of the American Chemical Society*, xxix., No. 10.

The following analyses of bromide-sulphocyanate mixtures were made according to the above directions :—

	N/15 KBr solution. Cc.	N/15 KCNS solution. Cc.	$AgNO_3$ equivalent of KBr taken.	$AgNO_3$ equivalent found.	Absolute error. Cc.
1.	25·00	0·15	22·72	22·76	+0·04
2.	25·00	0·15	22·72	22·69	−0·03
3.	25·00	3·00	22·72	22·73	+0·01
4.	25·00	5·00	22·72	22·78	+0·06
5.	25·00	10·00	22·72	22·69	−0·03
6.	25·00	10·00	22·72	22·68	−0·04
7.	25·00	25·00	22·72	22·73	+0·01
8.	25·00	50·00	22·72	22·74	+0·02
9.	25·00	100·00	22·72	22·72	0·00
10.	10·00	90·00	9·09	9·12	+0·03

4. *Theory of the Method.*

While the best test of a method is in its practical results, it is well to establish clearly the facts upon which it is based. Our method depends upon the following assumptions :—(1) That sulphocyanates may be decomposed at a temperature of about 100° by such concentrations of nitric acid as are insufficient either to oxidise chlorides or bromides, or to cause the volatilisation of hydrochloric or hydrobromic acid ; (2) that all but traces of the hydrocyanic acid formed by this decomposition can be volatilised during the time required for the oxidation itself ; (3) that the silver cyanide formed by addition of silver nitrate to this solution is sufficiently soluble in hot nitric acid to be separated quantitatively from the insoluble silver chloride by filtration ; and, finally, (4) that small amounts of silver cyanide do not interfere with the determination of the excess of silver by means of a sulphocyanate titration, since it acts as a soluble silver salt. Each of these assumptions has been subjected to experimental investigation.

The quantity of concentrated nitric acid used during the oxidation ordinarily amounts to 2 cc. or less. If acid should be added more rapidly than the decomposition of the sulphocyanate required, there can be present at any time not more than this small amount of acid in solutions the volume of which is usually about 200 cc. Experiments were therefore conducted to ascertain whether this amount of nitric acid could be used without loss of chlorine or bromine from solutions of the concentration used in our analytical method. 200 cc. samples of N/50 chloride solution, or N/100 bromide solution, were boiled gently for fifteen to twenty minutes with varying amounts of concentrated nitric acid, and the distillates, amounting in each case to about 15 cc., were carefully tested for the presence of the halogens. The experiments tabulated below were performed in duplicate :—

N/50 KCl. Cc.	Conc. HNO_3. Cc.	Vol. of distillate. Cc.	Cl present.
200	1·00	15	None
200	2·00	15	None
200	3·00	15	None
200	4·00	15	None
200	6·00	15	Traces

N/100 KBr. Cc.	Conc. HNO_3. Cc.	Vol. of distillate. Cc.	Br present.
200	1·00	15	None
200	2·00	15	None
200	3·00	15	None
200	3·50	15	Traces

The results show that under the conditions of analysis, loss of halogen cannot be caused by the addition of nitric acid and boiling.

The principal, but by no means the only, decomposition product of sulphocyanic acid is hydrocyanic acid. Tests showed that when a pure sulphocyanate is decomposed in the manner described, only traces of hydrocyanic acid remain in the solution ; when the decomposition is carried out in the presence of a chloride, amounts are retained corresponding to less than 2 mgrms. of silver cyanide. This rapid loss of hydrocyanic acid during twenty minutes' treatment appeared somewhat surprising in the light of Richards and Singers' observation that the presence of chlorides prevents the expulsion of hydrocyanic acid to a marked extent (*Am. Chem. Journ.*, 1902, xxvii., 208). It occurred to us therefore that the decomposition of the sulphocyanate might possibly result in the formation of cyanogen rather than hydrocyanic acid, as was suggested by Knüpffer (*Zeit. Phys. Chem.*, 1898, xxvi., 264), who oxidised the sulphocyanate with acid potassium iodate. Accordingly, the decomposition products were passed through a solution of potassium hydroxide and the alkaline liquid analysed ; it was found to contain cyanide but no cyanate, showing the absence of cyanogen, and indicating that we had in reality to do with a very rapid expulsion of hydrocyanic acid. Richards and Singer (*loc. cit.*) expressed the view that the retention of the hydrocyanic acid by chlorides might be due to the formation of ionic complexes. Assuming this interpretation to be correct, it would appear that the complex requires a measurable time interval for its formation, and that boiling will expel hydrocyanic acid from chloride mixtures much more rapidly at the time of its formation than after the solution has been allowed to stand. It would in all probability be a lengthy operation to volatilise the acid quantitatively, but this is unnecessary in connection with our method.

The solubility of silver cyanide in nitric acid of moderate strength, which is taken advantage of in our method of analysis, was noted by Gregor (*Zeit. Anal. Chem.*, 1894, xxxiii., 33), who showed the marked solubility of the cyanide in 6 to 10 per cent acid. In hot solutions of 25 per cent strength we find its solubility much greater ; at 80° about 0·5 cc. of N/15 potassium cyanide and 0·5 cc. of N/15 silver nitrate, corresponding to about 4 mgrms. of silver cyanide, can be added to 200 cc. of the acid without causing any turbidity. The amount of hydrocyanic acid left in the solution in our method is considerably less than the equivalent of this quantity of cyanide, and there is therefore no interference with the quantitative separation of the silver chloride from the decomposition products of the sulphocyanate by filtration of a hot nitric acid solution of 25 per cent strength.

That small amounts of silver cyanide can be left in the filtrate without interference with the determination of the total silver by means of a sulphocyanate titration might be expected from the fact that in acid solution silver cyanide is much more soluble than silver sulphocyanate. Consequently, the ammonium sulphocyanate added in the titration will decompose the silver cyanide in the sense of the equation $NH_4CNS + AgCN = AgCNS + NH_4CN$, and it will not be until the ammonium cyanide reaches a considerable concentration that the reverse action will become appreciable. To ascertain how great the concentration of cyanide might safely be allowed to become, the following experiments were conducted ; a silver nitrate solution of N/15 strength was standardised against an ammonium sulphocyanate solution, and to 15 cc. samples of the silver solution varying quantities of a N/15 potassium cyanide solution were added. In the presence of ferric iron as indicator, sulphocyanate was run into the solution until a strong red colour was obtained, the mixture was stirred briskly for five minutes to afford time for the decomposition of the silver cyanide, and then silver nitrate was run in drop by drop, with stirring, to the disappearance of colour. One drop more of the sulphocyanate gave in each case a permanent coloration. The quantity of sulphocyanate required for the total silver was then compared with the quantity as calculated from the original standardisation of the two solutions. The tabulated results show the variation in cc. from the true titre of the

solutions, the experiment being performed four times for each concentration of potassium cyanide used.

N/15 KCN taken in cc.	Extreme errors, in cc. of N/15 NH_4CNS.
0·10	−0·01 to −0·04
0·20	−0·01 to −0·06
0·30	+0·03 to −0·03
0·40	+0·05 to −0·01
0·50	+0·13 to +0·09
1·00	+0·52 to +0·12

The results show that quantities as great as 0·4 cc. of N/15 potassium cyanide solution do not affect the accuracy of the titration by amounts larger than the errors of measurement, while larger quantities cause perceptible errors in determining the true end-point. In the analytical method proposed, the amount of cyanide left in the solution is much less than half of this maximum amount.

Experiment thus substantiates the correctness of the assumptions involved in our method.

5. *Discussion of Existing Methods.*

A number of methods have been proposed for the analysis of mixtures of sulphocyanates and chlorides. The time-consuming method of Gondoin (*Zeit. Anal. Chem.*, 1897, xxxvi., 528), depending upon the precipitation and weighing of cuprous sulphocyanate, and that of Alt (*Ber.*, 1889, xxii., 3258: *Zeit. Anal. Chem.*, 1892, xxxi., 349), depending upon the oxidation of the sulphocyanate to sulphuric acid and its determination as barium sulphate, as well as the method of Krug and Ebroy (*Journ. Anal. Appl. Chem.*, vi., 184), depending upon the solubility of the salts in acetone, were not investigated.

Volhard proposed a volumetric method depending on the oxidation of the sulphocyanate by standardised potassium permanganate, assuming the correctness of the equation $NH_4CNS + 3O = NH_4CN + SO_3$ (*Ann.*, 1878, cxc., 1; *Zeit. Anal. Chem.*, 1879, xviii., 291). No analytical results accompany the publication of the method, which has nevertheless been incorporated in some text-books. An attempt to use this method resulted in complete failure. Taking a permanganate solution standardised against oxalic acid, and a sulphocyanate solution standardised against silver nitrate, effort was made to compare the two solutions by Volhard's method. The amount of sulphocyanate found varied from 86·2 per cent to 93·5 per cent of that actually present, in spite of the fact that conditions of concentration, temperature, and degree of acidity were kept as constant as possible. It was found impossible to obtain either uniformity or correctness of results. This same method has been proposed independently by Jumeau (*Bull. Soc. Chim.*, 1893, [3], ix., 346) and by Alt (*loc. cit.*), the latter stating that the method is inaccurate, but erroneously ascribing the irregularities to the iron usually present in commercial sulphocyanates.

Volhard (*Zeit. Anal. Chem.*, 1879, xviii., 291) also proposed decomposing the sulphocyanate by oxidation with dilute nitric acid at the temperature of the water-bath, then rendering the solution alkaline with ammonium hydroxide, evaporating to drive off the hydrocyanic acid quantitatively, and determining the chloride in the residual solution. Investigation of this method brought to our notice that, although the sulphocyanate is completely decomposed, as Volhard states, yet the subsequent treatment with alkali causes in part the re-formation of the sulphocyanate. This example of a reversible reaction becomes intelligible in the light of Stokes (*Journ. Am. Chem. Soc.*, 1907, xxix., 446), proof that a constant decomposition product of sulphocyanic acid is isopersulphocyanic acid, $H_2N_2C_2S_3$, which reacts with alkaline cyanides according to the equation $H_2N_2C_2S_3 + 3KCN = 3KCNS + 2HCN$. In like manner other compounds containing sulphur in the lower stages of oxidation react with cyanides to form sulphocyanates; *e.g.*, Gutmann makes the reaction of thiosulphates with potassium cyanide the basis of a method for the detection of thiosulphates (*Zeit. Nahr.-Genussm*, xiii., 261; *Chem. Centr.*, 1907, i., 1152; *Chem. Abstracts*, 1907, 1447). It is clear, therefore, that any method for the analysis of the mixtures under discussion will be faulty if the solution is rendered alkaline before complete oxidation of the sulphur, which operation was found by Treadwell to require two hours when the oxidising agent was fuming nitric acid ("Analytical Chem.," ii., p. 261, New York, 1906).

Borchers (*Zeit. Anal. Chem.*, 1883, xxii., 92; *Borchers' Repert. Anal. Chem.*, 1881, 130; Treadwell's "Anal. Chem.," ii., p. 261) proposes the precipitation of chloride and sulphocyanate as their silver salts, and the determination of their sum by Volhard's method; the precipitate is then washed into a flask with a stream of concentrated nitric acid, and boiled with that reagent for three-quarters of an hour to the complete decomposition of the silver sulphocyanate; the solution is diluted and filtered, and the silver determined in the filtrate. Experience showed that the long boiling with concentrated nitric acid renders the method entirely unsuited for ordinary laboratory use.

Barnes and Liddell (*Journ. Soc. Chem. Ind.*, 1883, ii., 122) precipitate the sulphocyanate as its cuprous salt by titration with copper sulphate in the presence of a bisulphite, the end-point of the reaction being determined by a drop test with potassium ferrocyanide. The authors note that the end-point cannot be determined exactly owing, as they state, to the oxidation of the copper in the cuprous sulphocyanate and its reaction with the ferrocyanide. We were unable to devise any method for rendering the determination of the end-point more exact, and found the method of use only for approximating the correct values.

Diehl (*Chem. Centr.*, 1883, 649; *Ber.*, 1883, xvi., 2319) also precipitates the sulphocyanate as its cuprous salt, using excess of copper sulphate and a bisulphite, filters off the precipitate, and determines the chloride in the filtrate. Noyes and Abbot (*Zeit. Phys. Chem.*, 1895, xvi., 129) investigated this method, and found variations between +0·27 per cent and −0·49 per cent in the amount of chlorides found; the method can therefore not be regarded as exact. Mann (*Zeit. Anal. Chem.*, 1889, xxviii., 668) has proposed a substitution of hydrogen sulphide for the bisulphite as a reducing agent; his results for the chloride vary from the true figures by −0·3 per cent to −2·8 per cent.

Incidentally to a physico-chemical research Knüpffer (*Zeit. Phys. Chem.*, 1898, xxvi., 262) proposed the oxidation of the sulphocyanate by acid potassium iodate. After boiling off the hydrocyanic acid, or cyanogen, as he believes it to be, he reduces the excess iodate with sulphur dioxide, oxidises with a nitrite, and boils again to expel the iodine completely; the chloride is determined in the residue. The figures given indicate that the method is accurate; it is made very tedious, however, by the repeated boilings necessary for quantitative expulsion of the hydrocyanic acid and the iodine.

The method of Rupp and Schied (*Ber.*, 1902, xxxv., 2191), depending upon the oxidation of the sulphocyanate by free iodine in bicarbonate solution and titration of the unused iodine, was shown by Thiele (*Ber.*, 1902, xxxv., 2766) to be inaccurate, owing to the incomplete oxidation of the sulphocyanate in the half-hour's time proposed by Rupp and Schied. Thiele states that if the oxidation be continued for four hours the results are accurate; in this modified form Rupp has adopted the method, and claims good results from its use (*Arch. Pharm.*, 1905, ccxliii., 468; *Journ. Am. Chem. Soc.*, 1906, xxviii., 1771; *Journ. Chem. Soc.* (Abstracts), 1905, lxxxviii., 867). In view, however, of Stokes' results on the decomposition of sulphocyanates and Treadwell's statement that complete oxidation to sulphuric acid requires the most vigorous treatment with fuming nitric acid, it may be doubted whether the oxidation by iodine follows quantitatively the simple equation expressed.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21st, 1907.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

(Concluded from p. 291).

236. "*Mercurous Hyponitrite.*" By EDWARD DIVERS.

A paper with the above title, by P. C. Rây, published in the August number of the *Transactions*, having been taken as read, opens with the following words: "Mercurous hyponitrite, which has already been obtained in a somewhat impure condition by the author (*Trans.*, 1897, lxxi., 348), may be prepared (*a*) by precipitating mercurous nitrate with carefully neutralised sodium hyponitrite made according to Divers' method (*Trans.*, 1889, lxxv., 96, 119); (*b*) by precipitating mercuroso-mercuric nitrite (Rây, *Trans.*, 1902, lxxxi., 644) with the crude alkaline hyponitrite; or (*c*) by precipitating mercurous nitrate with acid potassium hyponitrite (Thum, *Inaug. Dissert.*, 1893)." Any one unacquainted with the facts referred to will hardly get a correct notion of them from this obscure sentence. These facts are (1) that Thum, in an unusually brilliant inaugural dissertation on hyponitrous acid, gave, in 1893, a description, accompanied by excellent analyses, of the mercurous salt among others; (2) that, in 1897, there appeared a paper by Rây describing, as new, mercurous hyponitrite (in admixture with a mercuric salt) obtained from sodium hyponitrite by adding it to a solution of mercuroso-mercuric nitrite, a solution he had resort to (notwithstanding the complications likely to ensue consequent upon the presence in it of mercuric salt and upon its being a solution of a nitrite) because he supposed that mercurous nitrate would not serve for the purpose, in consequence of the acidity of its solution; and (3) that, beyond this pointless substitution of a solution of one mercurous salt for another, Rây's paper contained nothing new, nothing so good as had been already published, and yet something beneath criticism about a supposed mercuric hyponitrite (see *Trans.*, 1899, lxxv., 119).

Rây's recent paper, besides implying that mercurous hyponitrite, prepared by Rây's reagent, has now been obtained free from mercuric salt in some way not even alluded to (the evidence for this being some new analyses, three out of four of which are not a whit better than those of the admittedly impure preparations), contains only the statement that this preparation of Rây's (possibly containing nitrite) cannot be dissolved in nitric acid without immediately yielding metallic mercury, notwithstanding the fact that Thum was able to reprecipitate the salt in a pure state from its solution in nitric acid, as his analysis and description establish, and that the writer (*Trans.*, 1899, lxxv., 121) has published experience similar to Thum's, each working with salt of high purity.

237. "*Decomposition of Mercurous and Silver Hyponitrites by Heat.*" By EDWARD DIVERS.

Rây and Gañguli have not succeeded in giving a definite and consistent interpretation of the results which they have recorded in their recent paper on the decomposition of mercurous and silver hyponitrites by heat (*Trans.*, 1907, xci., 1397). They have not perceived that these results are impossible as they stand, and must be corrected if they can be. The corrections called for in the case of the silver salt lie well within the limits of errors in the experimental analyses, whilst, in the case of the mercury salt, the justifiable assumption of the presence of nitrite fairly well accounts for numbers otherwise too far from what the pure salt would have given. Had the authors been aware of the imperfect nature of their results, in the case of the mercury salt, they would presumably have deferred publication of them. But, even as published, these results seem capable of such revision and subsequent interpretation as may make them add materially to the knowledge of the decomposition of hyponitrites by heat.

The two hyponitrites examined evidently decompose when heated each in three ways, which are expressed by the following equations. For the mercury salt, these are: $(HgON)_2 = 2Hg + 2NO$ (1); $(HgON)_2 = Hg + HgO + N_2O$ (2); $3(HgON)_2 = 4Hg + (HgNO_3)_2 + 2N_2$ (3). In Rây and Gañguli's mode of procedure, it would seem, on probable calculation, as tabulated below, that 2·96 out of 6·09 parts of the salt will have decomposed according to (1), 2·32 parts according to (2), and 0·81 part according to (3). Or, in percentage numbers, 48·6, 38, and 13·3 according to Equations (1), (2), and (3) respectively.

In the case of the silver salt, where we are on much surer ground, two of the equations are just like (1) and (3) for the mercury salt, whilst the other, which only differs from (2) as given for the mercury salt because of the instability of silver oxide, is $(AgON)_2 = 2Ag + O + N_2O$ (2'), the free oxygen of which with 2NO by Equation (1) becomes first N_2O_3, let us say, and then nitrite, on contact with the solution of potassium hydroxide, as Rây and Gañguli explain. Ultimately, therefore, the second equation becomes $2(AgON)_2 = 4Ag + N_2O_3 + N_2O$, but, for the sake of comparison with the mercury salt, it seems better to use the equation showing free oxygen and count the nitrite nitrogen along with that as nitric oxide. The conclusion that must be come to, after inspecting the tables, will be that Rây and Gañguli had really 7·84 (6·58 + 1·26) parts out of 10·15 of the silver salt decomposed according to equation (1); 1·26 parts according to (2'), and 1·05 parts according to (3) (Ag being read for Hg). Or, 83, 13·3, and 3·7 per cent respectively according to Equations (1), (2'), and (3). Reference to the authors' paper will show that they have themselves put forward Equations (1) and (2), that they reject (3), and that they suggest others which, it may here be said, could not be worked in with their results in any likely way.

The interpretation, here submitted, of the effects of heating the two hyponitrites is derived from the numbers exhibited in the subjoined tables.

Distribution of the Nitrogen and Oxygen of Mercurous Hyponitrite in the Products of its Decomposition by Heat.

Product.	Found.		Calculated.	
	N.	O.	N.	O.
N_2	0·54	—	0·54	—
N_2O	2·32	1·33	2·32	1·33
NO	2·53	2·89	2·96	3·38
N_2O_3 ..	0·24	0·41	—	—
NO_3	0·48	1·65	0·27	0·92
HgO ..	—	1·19 (*a*)	—	1·33
Total ..	6·11	7·47	6·09	6·96
Theory.	6·09	6·96	6·09	6·96

Distribution of the Nitrogen and Oxygen of Silver Hyponitrite in the Products of its Decomposition by Heat.

N_2	1·06	—	0·70	—
N_2O	1·15	0·66	1·26	0·72
NO	6·58	7·52	6·58	7·52
N_2O_3 ..	1·26	2·16	1·26	2·16
NO_2 ..	0·35	1·20	0·35	1·20
Total ..	10·40	11·54	10·15	11·60
Theory.	10·15	11·60	10·15	11·60

(*a*) See note on p. 1400 in Rây and Gañguli's paper.

The numbers in the first column of each table are the mean numbers of those given by the authors for the nitrogen of the several products as parts per cent of the salt. The fourth line ("N_2O_3") shows the nitrogen of the nitrite in the potassium hydroxide solution they made use of. The fifth line ("NO_3") shows the nitrogen, obtained or calculated, as mercurous or silver nitrate. In the case of the mercurous hyponitrite, the distribution of the nitrogen

as nitrite and nitrate has been assumed to have been in all three experiments as 1 : 2, in agreement with what it was found to be in the only reported experiment in which it was determined by the authors.

The numbers in the second column of each table are for the oxygen corresponding with those for the nitrogen in the first column. Their sum, in the case of the mercury salt, is much in excess of the percentage of oxygen in mercurous hyponitrite. Since the mercurous hyponitrite, which the authors made use of, had been prepared from mercuroso-mercuric nitrite, the excess of oxygen found may be attributed to the presence of nitrite in the salt as prepared. The sixth line ("HgO") shows the oxygen left as mercuric oxide as being necessarily equal to that in the nitrous oxide, less (in the second column) by one-third of that as nitrous anhydride (1·33 – 0·14 = 1·19).

The numbers in the third and fourth columns of each table have been calculated in accordance with the equations already given, and in such a way as to make them differ the least possible from the numbers furnished by the experiments, under the necessary condition that their respective sums shall be identical with the percentages of nitrogen and oxygen in the pure mercurous and silver hyponitrites. In the case of the mercury salt, it has been assumed that, when free from nitrite, mercurous hyponitrite yields no red fumes and very little nitrate, which is in accordance with the writer's experience, referred to by the authors. The numbers for the silver salt have been altered to make the free nitrogen equal to only twice that found as nitrate; that found as nitrous oxide to be equal to that as nitrite, and total nitrogen and oxygen to be equal respectively to the percentages of these elements in the pure salt.

A noticeable point in Rây and Gañguli's paper is their experience of the conversion by heat of nearly one-eighth of silver hyponitrite into silver, nitrous oxide, and oxygen. The writer did not observe the presence of any nitrous oxide in his experiments (*Trans.*, 1899, lxxv., 108). Nor has any other worker recorded the fact of having done so. On the evidence afforded by Rây and Gañguli's experiments, the writer is prepared to admit that nitrous oxide may never be absent altogether in the products of the decomposition of silver hyponitrite by heat. As to the matter of quantity of nitrous oxide, the details of their experiments and his are sufficiently different to account for the fact of their obtaining so much of it and he so little as to pass unnoticed. The salt they used contained, they think, impurities enough to be mentioned, and began to decompose very slowly at 100°, and at 140° suffered rapid decomposition. It had been dried cold over sulphuric acid under reduced pressure, but was heated to decomposition in a tube between which and the Sprengel pump a tube of "aqueous potash" intervened. A very little moisture would have given a lower temperature of decomposition, and caused free generation of nitrous oxide. In the writer's experiments, salt of high purity, dried finally in a Sprengel vacuum at 98°, was used. Thus dried, the pure salt hardly begins to decompose at 140°, and is not in free decomposition much, if at all, below 160°. It would seem highly probable from the difference in the effects of heat that the generation of nitrous oxide is largely, if not wholly, a matter of hydrolysis.

Another point worthy of attention in Rây and Gañguli's paper is their contention that nitric peroxide is a secondary product arising out of the union of nitric oxide with the oxygen set free along with nitrous oxide. The writer thinks this to be highly probable. His position as to nitric oxide and nitric peroxide being primary products has been that for twenty years he held, without proof, that nitric oxide was the primary product which produced red fumes by contact with air. Thum proved, in 1893, that out of contact with air the salt still gave nitric peroxide when heated. The writer then examined the matter himself for the first time and found Thum right. Having ascertained that nitric peroxide and silver gave silver nitrate and nitric oxide, he concluded, in 1899, that nitric peroxide was the primary product and nitric oxide secondary. Now he returns to his first view and agrees with Rây and Gañguli that nitric oxide is the primary product, at the same time being certain that it is also reproduced by reduction of the nitric peroxide by silver.

It is much to be desired that Rây and Gañguli would repeat their experiments, making use of pure mercurous hyponitrite prepared by Thum and the writer's process, and of the driest pure silver hyponitrite, in their apparatus supplied with some solid potassium hydroxide in the near end of their absorption tube.

238. "*Cupric Nitrite.*" By EDWARD DIVERS.

A paper appeared not long ago in the *Transactions* (1907, xci., 1405) on cupric nitrite, in which Rây sets forth his observations on what he regards as being the atmospheric oxidation and autoxidation of this salt. Now nitrites, as such, do not oxidise, and, in the cases where they do not hydrolyse in water, they are stable in solution. (The passage of cobaltous into cobaltic nitrite is, of course, no exception to the statement.) What Rây has occupied himself with is simply the oxidation of nitrous acid, not cupric nitrite, in aqueous solution. For when a cupric salt is dissolved in water, it is always hydrolysed to some extent, as is shown by its acid reaction and other facts. Nitrous acid in aqueous solution becomes nitric acid and nitric oxide, and nitric oxide oxidises in the air. When it is added that nitric acid decomposes some of the cupric nitrite to form nitrate together with more free nitrous acid, there seems to be no more to be said. As to the oxidation of cupric nitrite, as such, we are left as we were, without any evidence whatever of its occurrence.

NOTICES OF BOOKS.

Steel Works Analysis. By JOHN OLIVER ARNOLD and F. IBBOTSON. Third Edition. London and New York: Whittaker and Co. 1907.

THIS book is intended specially for the use of assistants in steel works, and for students who wish to fit themselves for posts in steel works' laboratories, or who, having a fair knowledge of pure chemistry, wish to specialise in the analytical investigation of irons and steels. Only those processes are discussed which give accurate results, and a great choice of methods is avoided in favour of the plan of giving only one or two really reliable methods of determining each important constituent. The description of each process is clearly arranged in such a way that the student is practically forced to keep the theoretical reason for every step well in mind, and preserved from merely adding certain reagents or subjecting his sample to specified operations mechanically. The approximate time taken for each experiment is stated. In the third edition gas analysis is treated more fully than before, and the section on the calorimetry of fuels has also been enlarged and brought up to date. In addition the analysis of brasses, bronzes, and white metals is now included, and every part of the book has been carefully revised.

Electric Power and Traction. By F. H. DAVIES, A.M.I.E.E. London: Archibald Constable and Co., Ltd. 1908.

A KNOWLEDGE of the possibilities of electric traction and the application of electric power in general has become almost indispensable to many classes of students, members of allied trades, and engineers, and this book will fulfil a useful purpose if it enables such readers to get a practical insight into the generation and distribution of power and its application under various circumstances. The author appears to have chosen his subjects exceedingly well, and has contrived to make his book interesting, while at the same time he has not entirely avoided technical details. The various systems adopted in electric traction are fully

discussed and illustrated, and the advantages and disadvantages of three-phase and one-phase motors are weighed. A useful glossary of the terms which might possibly be unfamiliar to the student who has not had any special training in electrical engineering adds greatly to the usefulness of the book.

A History of Hindu Chemistry. By Praphulla Chandra Ray, D.Sc. Second Edition. London: Williams and Norgate. 1907.

The second edition of this work, which had a very favourable reception at the hands of orientalists and others, contains some important additional matter which shows clearly that the sciences of chemistry and medicine were developed earlier among the Hindus than among the Greeks. The book contains copious quotations from Sanskrit texts, and the author has collected valuable information from rare manuscripts relating to the origin of Hindu chemistry. The book is one which hardly appeals to the general student of chemical history, but at the same time the author's acquaintance with scientific knowledge among the Hindus is probably unique, and his book will command the attention of all who are making a special study of the early history of the science.

La Bibliographie Industrielle. ("The Industrial Bibliography.") By Jules Garçon. Paris: 40 bis, Rue Fabert. 1907.

This essay on the practical value of a scientific and industrial bibliography gives many examples of the hindrances which the lack of a comprehensive and classified index puts in the way of scientific work, and shows clearly what great benefits such an index would confer on inventors and others. There is no need for the author to emphasise the many difficulties which those who want to look up some special question encounter when they are forced to consult the scattered literature in different languages which may contain references to the work they have in hand, and it is universally recognised that a trustworthy index would be a great convenience. In the essay suggestions are made as to the most satisfactory basis of a complete bibliography, and details of the best arrangement and division of subjects are included, with some hints about the preparation of summaries of the papers catalogued.

CORRESPONDENCE.

ALUMINIUM CARBIDE.

To the Editor of the Chemical News.

Sir,—My attention has been drawn to a letter on the subject of aluminium carbide, by Messrs. Ellis and Weston, which appeared in the Chemical News of November 29th (vol. xcvi., p. 270).

Having carried out in the Electro-chemical Laboratory of Dr. Hutton, Manchester University, in the autumn of 1904 and subsequently, an extended investigation of the formation of this compound, I should like to point out that, although the formation of aluminium carbide was carried out in a variety of ways and at different temperatures, no evidence was obtained of the existence of any other carbide than that represented by the formula Al_4C_3. The only gases evolved from the product on treatment with dilute HCl were methane and hydrogen, the latter from the unchanged aluminium, with only a trace of other gases due to impurities in the aluminium, such as always give an odour to hydrogen evolved when acids act on metals. My experiments were chiefly carried out to find the *rôle* played by carbon monoxide in the formation of carbide.—I am, &c.,

W. H. Patterson.

Heriot-Watt College, Edinburgh.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 21, November 18, 1907.

Presence of Paramethoxycinnamic Aldehyde in Essence of Tarragon, and some Derivatives of Tarragol.—Maurice Daufresne.—Essence of tarragon, on repeated fractionation under reduced pressure, gives a yellow oil, which in all its reactions resembles paramethoxycinnamic aldehyde, $O.CH_3—C_6H_4—CH = CH—CHO$. The same aldehyde can be prepared by condensing anisic aldehyde and acetaldehyde in presence of caustic soda. The fixation of one molecule of hypoiodous acid by tarragol in presence of ether which has been freed from alcohol and saturated with water, leads to the formation of the monoiodohydrine of *p*-methoxyphenylpropane diol, $O.CH_3—C_6H_4—CH_2—CH.OH—CH_2I$. When tarragol is subjected to the action of iodine and mercuric oxide in absolute methyl alcohol the methyl iodohydrine is formed, $O.CH_3—C_6H_4—CH_2—CH(O.CH_3)—CH_2I$.

No. 22, November 25, 1907.

Nitrous Isomerisation of Isobutyl Alcohol.—Louis Henry.—By the action of metallic nitrites upon the chlorhydrate isobutylamine is converted into a mixture of which three quarters is tertiary butyl alcohol and one quarter isobutyl alcohol. The methylated homologues of the salts of ethylamine under the same conditions invariably give alcohols which do not correspond exclusively to the amine used, and the quantity of alcohol produced by this isomerisation increases in proportion as the methylic substitution is more complete; *i.e.*, as the hydrogen is scarcer in the system adjacent to the complex $H_2C—(NH_2)$, at the expense of which the alcohol, the final product of the reaction, is formed. This nitrous isomerisation of alcohols is analogous in many ways to the isomerisation of haloid ethers under the action of heat.

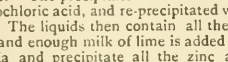
Uranium Tetraiodide.—Marcel Guichard.—The author has prepared the anhydrous tetraiodide of uranium in sealed exhausted tubes by heating iodine to 180° and letting the vapour act upon uranium heated to 500°. The iodide is a crystalline mass, fusing at about 500°. Its specific gravity is 5·6 at 15°. When heated in hydrogen it gives up iodine. Chlorine decomposes it in the cold. When it is heated gently in dry oxygen it takes fire, and is converted into the green oxide, U_3O_8. The same reaction occurs when it is heated in dry air. It also loses iodine, and absorbs oxygen when kept at the ordinary temperature in dry air. In damp air it deliquesces and forms a brown liquid, which contains free iodine, and if after some hours excess of water is added a yellow solution is obtained which when heated gives a precipitate of green hydrated oxide. The tetraiodide dissolves easily in water, and in absence of oxidising agents gives a green acid solution. The analysis of the iodide agrees closely with the formula UI_4.

Synthesis of Ammonia from its Elements by Catalysis.—Léon Brunel and Paul Woog.—The authors prepared mixtures of nitrogen and hydrogen (1 vol. to 3 vols.), and passed them at different temperatures and with different velocities over substances which would be likely to act as catalysers. With finely-divided carbon, obtained by the decomposition of toluene or carbon dioxide by reduced nickel, no ammonia is formed between the temperatures of 170° and 285°. But if under the same conditions the nitrogen in the gaseous mixture is replaced by air a certain amount of carbon burns, and the heat disengaged by this reaction leads to the formation of small quantities of ammonia.

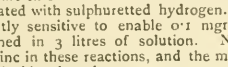
Method of Determining very Small Quantities of Zinc.—Gabriel Bertrand and Maurice Javillier.—A complex mixture of Sn, Sb, As, Cu, Cd, Co, Pb, Ag, Fe, Mn, Zn, Al, Ba, Ca, Mg, Na, K as carbonates, chlorates, sulphates, nitrates, phosphates, silicates, and sulphides, is treated with aqua regia, evaporated, taken up with dilute hydrochloric acid, and precipitated with sulphuretted hydrogen. The filtrate is boiled, ammonia is added and hydrogen peroxide. The precipitate which forms is again dissolved in hydrochloric acid, and re-precipitated with ammonia and H_2O_2. The liquids then contain all the zinc. They are boiled, and enough milk of lime is added to liberate all the ammonia and precipitate all the zinc as zincate. The calcium zincate is treated with hydrochloric acid, thus giving zinc chloride and calcium chloride, and the zinc is precipitated with sulphuretted hydrogen. This method is sufficiently sensitive to enable 0·1 mgrm. of zinc to be determined in 3 litres of solution. Nickel and cobalt follow zinc in these reactions, and the method is therefore not applicable when they are present.

Two Isomeric Methyl Sparteins.—Charles Moureu and Amand Valeur.—Two definite chemical products can be isolated by decomposing the hydrate of α-methyl sparteinium. When the mixture of the products is treated with methyl iodide 30 per cent does not undergo methylation. This part is α-methyl spartein. β-Methyl spartein is transformed into iodo-methylate from which it is difficult to isolate the base. The fractional crystallisation of the di-iodohydrates prepared from the raw base enables the separation of the less soluble α-methyl spartein di-iodohydrate to be effected quite easily. If the raw base is heated on a water-bath with a slight excess of normal sulphuric acid, only the sulphate of α-methyl spartein isomerises to sulphomethylate, and the action of alkali liberates the bases which have not isomerised. By fractionating the mono-iodohydrates of these last bases a definite mono-hydrate can be isolated, and from it β-methyl spartein can be extracted. α- and β-Methyl sparteins are unsaturated bases which energetically reduce potassium permanganate in acid solution at 0°. In both of them the methyl group is bound to the nitrogen. They differ essentially from one another in the fact that α-methyl spartein alone isomerises under certain conditions to saturated derivatives.

Synthesis of β-Campholene Lactone from the Lactone of 2—4-Dimethyl 2-Cyclopentanol 1-Acetic Acid.—G. Blanc.—Methyl β-methyl adipate condenses under the action of sodium, giving methyl cyclopentanone carbonic esters of formula—



The sodium derivative of this ester yields the condensation product—



when treated with ethyl bromacetate. This compound is hydrolysed by boiling hydrochloric acid to 4-methyl 2-cyclopentanone 1-acetic acid, the methyl ether of which yields β-campholene lactone.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 14, 1907.

Hydroxy - aquo - tetrammino - colbatic Salts.—A. Werner.—Diaquo-tetrammino-cobaltic chloride when dissolved in concentrated ammonia and precipitated with alcohol readily gives the hydroxy salt, $\left[\begin{matrix}HO\\H_2O\end{matrix}Co(NH_3)_4\right]Cl_2$, from which other salts of the same series can be prepared. They are bluish or reddish purple in colour, and have an alkaline reaction in aqueous solution. With ammonium salts they give diaquo-tetrammino-cobaltic salts,—

$$\left[\begin{matrix}HO\\H_2O\end{matrix}Co(NH_3)_4\right]X_2 + NH_4X = \left[\begin{matrix}H_2O\\H_2O\end{matrix}Co(NH_3)_4\right]X_3 + NH_3.$$

They are unstable in aqueous solution, their colour changing in a short time to red-brown, which finally darkens, and black or brown crystals of the dodecammino-hexol-tetra-cobaltic series, $\left[Co\left[\begin{matrix}HO\\HO\end{matrix}Co(NH_3)_4\right]_3\right]X_6$, separate.

Hydroxy - nitro - tetrammino - cobaltic Salts. — A. Werner.—The aquo-nitro-tetrammino-cobaltic salts give with ammonia the following reaction :—

$$\left[\begin{matrix}H_2O\\O_2N\end{matrix}Co(NH_3)_4\right]X_2NH_3 = \left[\begin{matrix}HO\\O_2N\end{matrix}Co(NH_3)_4\right]X + NH_4X.$$

The chloride, nitrate, and bromide of this latter series all crystallise with 1 molecule of water. Their aqueous solutions are alkaline, and they absorb carbon dioxide from the air when moist, the following reaction occurring in the case of the nitrate :—

$$\left[\begin{matrix}HO\\O_2N\end{matrix}Co(NH_3)_4\right]NO_3 + CO_2 = \left[\begin{matrix}HO_2CO\\O_2N\end{matrix}Co(NH_3)_4\right]NO_3.$$

This reaction shows that the constitution of the salt is correctly represented by the formula. If it were an aquo - salt the reaction would be $\left[\begin{matrix}H_2O\\O_2N\end{matrix}Co(NH_3)_4\right]\begin{matrix}OH\\NO_3\end{matrix} + CO_2 = \left[\begin{matrix}H_2O\\O_2N\end{matrix}Co(NH_3)_4\right]\begin{matrix}CO_3H\\NO_3\end{matrix}$. and the carbon dioxide ion could be detected in the resulting product, which is not the case.

Anomalous Inorganic Oxonium Salts ; a New Class of Basic Salts.—A. Werner.—The author has already described two classes of basic salts, namely, those in which the hydroxyl groups are bound non-ionogenically with the metallic atoms, *e.g.*, $\left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]X_2$, and, secondly, the *ol*-salts, in which the hydroxyl group forms a link between two metallic atoms, *e.g.*, $\left[Co\left[\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right]_3\right]X_6$. When either ammonium chloride, iodide, or bromide acts on the hydroxy-nitro-tetrammino-cobaltic salts a third series of salts, *e.g.*, $\left[Cl(H_3N)_4Co\begin{matrix}OH\\NO_2\end{matrix}\right]_2HCl + 4H_2O$, is obtained. These salts resemble the anomalous organic oxonium salts, and their existence is an important argument against the assumption of tetravalent oxygen in oxonium salts.

Chloro - nitro - tetrammino - cobaltic Salts. — A. Werner.—Chloro - nitro - tetrammino - cobaltic chloride is very rapidly hydrated when dissolved in water, and even if nitric or sulphuric acid is immediately added only aquo salt can be separated. If, however, the chloride is poured on to a filter with ice-cold water, and the filtrate is allowed to drop into the cooled reagent, the hydration process can be arrested, and chloro-nitro-tetrammino salts separate. Thus it has been found that the chloride precipitated by potassium chloride from a solution of aquo-nitro-tetrammino salts is an esohydrate of chloro-nitro-tetrammino-chloride, *i.e.*, $\left[\begin{matrix}Cl\\O_2N\end{matrix}Co(NH_3)_4\right]Cl + H_2O$. (An esohydrate is one in which the water molecule does not form part of the inner nucleus of the complex radiele). Aquo compounds are the more unstable the more strongly basic is

the hydroxy compound in aqueous solution, as the following scheme shows :—

$$\left[\begin{matrix}O_2N\\Cl\end{matrix}Co(NH_3)_4\right]Cl_2 + H_2O \rightleftarrows \left[\begin{matrix}O_2N\\H_2O\end{matrix}Co(NH_3)_4\right]Cl_2;$$

Very quickly.

$$\left[\begin{matrix}O_2N\\HO\end{matrix}Co(NH_3)_4\right]Cl.$$ Strong base ; precipitates AgO.

$$\left[\begin{matrix}Cl\\H_2O\end{matrix}Co(NH_3)_4\right]Cl_2 + H_2O \rightleftarrows \left[\begin{matrix}H_2O\\H_2O\end{matrix}Co(NO_3)_4\right]Cl_3;$$

Much more slowly.

$$\left[\begin{matrix}H\\H_2O\end{matrix}Co(NH_3)_4\right]Cl_2.$$ Weaker base ; sets NH_3 free from ammonium salts.

$$\left[\begin{matrix}Cl\\ON\end{matrix}Ru(NH_3)_4\right]Cl_2 + H_2O \rightleftarrows \left[\begin{matrix}H_2O\\ON\end{matrix}Ru(NH_3)_4\right]Cl_3;$$

Exceedingly slowly.

$$\left[\begin{matrix}HO\\ON\end{matrix}Ru(NH_3)_4\right]Cl_2.$$ Neutral.

$$\left[\begin{matrix}Cl\\Cl\end{matrix}Pt(NH_3)_4\right]Cl_2 + H_2O \rightleftarrows \left[\begin{matrix}H_2O\\H_2O\end{matrix}Pt(NH_3)_4\right]Cl_4;$$

Does not take place.

$$\left[\begin{matrix}HO\\HO\end{matrix}Pt(NH_3)_4\right]Cl_2.$$ Neutral.

This explains why salts such as potassium chloride and sodium chloride undergo a momentary electrolytic dissociation when they dissolve in water, although they always separate from solutions in the anhydrous form. In these chlorides, which are derived from the strongly basic alkaline hydroxides, the processes of hydration and dehydration take place so quickly that they cannot be detected by any known method.

Theory of Bases.—A. Werner.—One of the most important results of the author's investigation of the hydroxy metallic ammonia compounds is the discovery that these compounds are simply special cases of the group of metallic hydroxides, and behave like salts ; *i.e.*, the hydroxyl groups bound directly to the metal cannot be ionised, and the electrolytically dissociated part of the hydroxy compounds is present in aqueous solution as hydroxide of the aquo-compound :—

$$\left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]Cl_2 + H_2O \rightarrow \left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]\begin{matrix}OH\\Cl_2\end{matrix}.$$

Hydroxy-compound (OH non-dissociating). Aquo-compound (OH dissociating).

The hydroxy compound may be called an anhydro-base and the aquo compound an aquo-base. Then any compound which combines with water to give a hydrate, which dissociates in aqueous solution into a complex positive ion and hydroxyl ions, is an anhydro-base, while all water addition products giving hydroxyl ions in aqueous solution are aquo or true bases. The stability of the aquo salts varies with the nature of the acid radicle and of the base, and generally the aquo salt is more unstable the stronger the acid is.

Behaviour of Sulphur towards Water, and the Vapour Pressure of Sulphur from 78° to 210°.—Otto Ruff and Hugh Graf.—To investigate the behaviour of sulphur towards water vapour the authors have compared the partial pressure of sulphur in an indifferent gas and in water vapour. If a reaction with water occurs according to the equation $2H_2O + S_3 = 2H_2S + SO_2$, as Cross and Higgin state, the partial pressure in water vapour would be greater than in an indifferent atmosphere. Carbon dioxide was used to test this statement, and the vapour pressures were measured between 78° and 210° by the dynamical method. It was found that the partial pressures in water vapour and in carbon dioxide were the same, and that consequently there can be no appreciable reaction between sulphur and water. The following table shows the vapour pressures at different temperatures :—

Temperature.	Vapour pressure.
78°	0·002 mm.
104°	0·01 ,,
135°	0·1 ,,
181°	1·0 ,,
245°	10 ,,

MEETINGS FOR THE WEEK.

Saturday, 28th.—Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Astronomy, Old and New," by Sir David Gill, K.C.B., F.R.S., &c.

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2509.

THE ESTIMATION OF CELLULOSE IN WOOD BY THE CHLORINATION METHOD.

By A. L. DEAN and G. E. TOWER.

The chemical constitution of woody tissues presents a problem of great complexity. Any single sample of wood contains a number of complex compounds whose nature is but little understood. If all kinds of wood were chemically alike, or even if the wood from all parts of the same tree was identical, the study of woody tissue would be simplified. The older idea, especially the idea prevalent amongst botanists, was that the cell walls of woody tissues were composed of "cellulose" which became impregnated with "lignin." Later and more careful studies appear to have established the fact that the foundation of woody cell walls is not a simple cellulose, but a compound cellulose, to which the name lignocellulose has been given. This lignocellulose may be split up into cellulose on the one hand and the lignone group on the other. The cellulose which results from the cleavage differs to a marked extent from the normal type cellulose of the cotton fibre. The lignone complex appears to contain cyclical groups and to be related to the carbohydrates in no very definite fashion.

Besides the lignocellulose which makes up the major portion of wood, there are always present a number of different bodies which are apparently not chemically united to the lignocellulose. Amongst these substances two are prominent; the so-called wood gum, which may be extracted with cold dilute alkaline solutions, and the group of the ether soluble resins.

It was stated above that the lignocellulose might be split into the two constituent radicals, cellulose and lignone. This cleavage is not easily carried out quantitatively, inasmuch as the treatments which remove the lignone tend to attack the cellulose. The isolation of cellulose from wood is carried out on an enormous scale in the manufacture of paper-pulp by the sulphite and soda processes. These methods are said to always involve some loss of cellulose, and unless carefully regulated the loss is likely to be great.

A number of methods have been elaborated for the estimation of the quantities of cellulose in vegetable cell walls. They are all tedious, and the cellulose obtained by several of them is apparently a variable and ill-defined product. Cross and Bevan have elaborated a method for the estimation of cellulose in the lignocellulose of jute fibre, a method which appears to yield concordant and valuable results ("Cellulose—an Outline of the Chemistry of the Structural Elements of Plants," Cross and Bevan, London, 1895). In their method the lignocellulose is treated with chlorine gas, giving rise to a lignone chloride which is soluble in hot alkaline sulphite solutions. They do not give the results of the systematic application of this method to cellulose estimations in wood, although they imply that it is applicable to such tissues.

Sherman (*Journ. American Chem. Soc.*, 1897, xix., 291), in his study of the insoluble carbohydrates of the wheat, estimated the amount of cellulose in the lignocellulose of the wheat kernel. After trying out the methods of Schulze (potassium chlorate and nitric acid), Lange (fusion with caustic alkalis), and the chlorination method of Cross and Bevan, Sherman concludes that this last method gives the most exact estimate of the cellulose and yields cellulose of maximum purity.

Cross and Bevan give the following directions ("Cellulose," p. 95):—"About 5 grms. of the fibre weighed after drying at 100° are—(*a*) boiled for thirty minutes with a dilute solution of sodium hydrate (1 per cent NaOH), which is kept at constant volume by addition of water. The fibre is well washed on a cloth or wire gauze filter, squeezed to remove excess of water, opened out, placed in a beaker, into which (*b*) a slow stream of washed chlorine gas is passed. Rapid reaction ensues, and the fibre changes in colour from brown to a bright golden yellow. To ensure complete conversion of the lignone, it is necessary to leave the fibre for some time (from thirty to sixty minutes) in the atmosphere of Cl gas. (*c*) The chlorinated fibre is removed, washed once or twice with water to remove hydrochloric acid, and placed in a 2 per cent solution of sodium sulphite; the solution is gradually raised to the boiling point, a small quantity of caustic soda solution is added (0·2 per cent NaOH calculated on the solution), and the boiling continued for five minutes. (*d*) The cellulose is now thrown upon a cloth filter, and washed with hot water. It will be found to be almost pure, *i.e.*, white; but to remove the last residues of the non-cellulose, it may be bleached by immersion in a dilute solution by hypochlorite (0·1 per cent NaOCl) for a few minutes, or treated with dilute permanganate solution (0·1 per cent $KMnO_4$). It is well washed from these oxidising solutions, treated with sulphurous acid on the filter, well washed with water, squeezed, dried, and weighed.

In another place these authors state that in applying this process to wood, it is necessary to reduce the wood "to the finest possible shavings." In giving directions for obtaining cellulose from pine wood (*loc. cit.*, p. 244) they say that after treating the finely divided wood as in the above quoted passage, the chlorination must be repeated until pure cellulose is obtained.

It is, of course, impossible to follow the directions given above when using finely ground wood, since the quantitative removal of such a material from a gauze or cloth filter, without the use of a stream of water, is practically impossible. After some experimenting we adopted the following method of procedure.

The wood was dried out at a low temperature, 60—80°, and ground in a hand mill. The material was then sifted through a sieve having twenty-four meshes to the inch. The wood powder obtained in this way was dried at 100—105°, and weighed portions of about 5 grms. each used for each determination. The sample, after being boiled in 200 cc. of 1 per cent sodium hydroxide solution for a half-hour, was filtered with suction on a small perforated porcelain plate in a five-inch funnel. In order to hold the plate firmly in the funnel during the filtration and the subsequent manipulation, we passed a piece of fairly stiff silver wire up through one of the holes in the centre of the plate and securely fastened it by bending the end down. The silver wire extended down through the stem of the funnel, projecting a quarter of an inch beyond the end. By putting one or two slight bends in the wire it can be made to bear against the walls of the inside of the stem, and the filter plate is held firmly in place. When the ground wood is first poured on to such a plate it behaves much like asbestos, some running through and the rest matting down and forming a coherent layer. The portions running through are then poured back, and by careful manipulation no significant loss of fibre occurs. The wood which had been boiled in alkali was washed on the filter with a large volume of water. The matted fibre was loosened up with a sharp pointed glass rod, and the rubber tube leading from a chlorine generator attached to the stem of the funnel. A slow stream of washed chlorine gas was passed up through the material, which was occasionally stirred to allow a thorough penetration of the gas.

After the chlorination the funnel was returned to the suction flask and the fibre washed to remove hydrochloric acid. For the boiling in sodium sulphite solution it was necessary to remove the material to a casserole. This may be readily accomplished by inverting the funnel over the casserole and pushing on the silver wire projecting

TABLE I.

Wood	Length of chlorination.	Appearance of cellulose.	Per cent of cellulose.	Per cent gain with ferrocyanide reaction.
Longleaf pine—Sapwood ..	2 chlorinations of 1 hour and ½ hour	Cream colour	53·5	
,, ..	4 ,, of ½ hour each . ..	White	53·8	
,, ..	2 ,, ,, ,, . ..	Light cream (uneven)	58·4	
Heartwood (*a*)	3 ,, ¾, ¾, and ½ hour ..	White	45·8	
,, ..	3 ,, ,, ,, ..	Light cream	49·0	
,, ..	3 ,, ,, ,, ..	Dark	52·8	
Loblolly pine—Sapwood . ..	3 ,, ½ hour each	Dark	60·8	
,, ..	2 ,, ,, ...	Dark	63·3	
,, ..	3 ,, ½ hour and 1 of ¾ hr.	White	53·9	
,, ..	2 ,, ,, ,,	White	54·5	
Heartwood (*a*)	2 ,, ¾ hour and 1 of ½ hr.	Light cream	49·6	3·80
,, ..	3 ,, ¾ hour	Light cream	48·1	2·69
Lodgepole pine—Sapwood ..	2 ,, ,, ...	Light cream	59·4	6·71
,, ..	2 ,, ,, ...	Light cream	58·8	4·18
Heartwood .	3 ,, ¾ hour and 1 of ½ hr.	White	43·7	2·36
,, ..	3 ,, ,, ,,	Very white	40·4	4·05
,, ..	2 ,, ¾ hour	Cream colour	49·5	−0·59
,, ..	2 ,, ,, ...	Cream colour	50·4	−3·77
Spruce—Mixed heart and sap.	2 ,, ½ hour and 1 of ¾ hr.	Light cream	59·6	3·94
,, ,,	2 ,, ½ hour	Dark	63·8	6·07

(*a*) In boiling with Na_2SO_3 after the first chlorination of this sample, the solution was made alkaline to 0·4 per cent instead of the usual 0·2 per cent.

from the stem. The main mass of the material drops out and the remainder is readily washed from the funnel and filter plate with the aid of 150 cc. of 2 per cent sodium sulphite solution which has been previously measured into a wash-bottle. After bringing the sulphite solution to a boil, 3 cc. of a 10 per cent sodium hydroxide solution were added and the mixture boiled for five minutes. The fibre was again collected on the filter plate, washed with hot water until the washings were colourless, and the product again chlorinated, or, when desired, bleached in the funnel by the use of 0·1 per cent potassium permanganate solution followed by sulphurous acid. In order to conveniently weigh the final product it was transferred from the funnel to a beaker, with the aid of alcohol from a wash-bottle, and then collected in a large, tared Gooch crucible, dried, and weighed.

A single chlorination, even if prolonged for two hours, was insufficient to yield a white cellulose after permanganate bleaching. The greatest difficulty in the whole process lay in judging the end-point. Finely ground wood is not homogeneous, since there are always small pieces made up of cells from the summer wood of the annual rings, and these cells with their thick walls offer a marked resistance to reagents. It frequently happened that after a series of chlorinations and permanganate bleachings which reduced the great mass of the sample to white cellulose that there still remained particles which were yellow. Since treatment with chlorine gas will attack wood cellulose to some extent, it became questionable whether or not continued chlorination did not cause a loss of cellulose in the finer particles which introduced a greater error than that caused by stopping the treatment before the sample was uniformly white.

The lignocelluloses when immersed in a mixture of equivalent solutions of potassium ferricyanide and ferric chloride are stained blue with the fixation of both iron and cyanide groups. The gain in weight occurring in this reaction varies with the quantity of ferric ferricyanide solution which is used. Sherman found that with the same volumes and strengths of solutions, and the same time of immersion, the gain in weight was constant for a given sample. By applying the reaction to the cellulose obtained by the different methods, he obtained a criterion of their purity. Of the use of the reaction he says (*loc. cit.*, p. 304), "The reaction with the ferricyanide solution seems of considerable value in testing the purity of celluloses. When the sample increases only slightly (about 1 per cent or less) in weight and is dyed only a bluish-green instead of a deep blue colour, it is at least a very strong indication that lignin substances are not present in notable quantity."

In applying this reaction to the products obtained by us, we have followed Sherman's procedure :—10 cc. of 1·6 per cent solution of ferric chloride were mixed with 10 cc. of a freshly prepared 3·3 per cent solution of potassium ferricyanide; to this mixture 1 grm. of dry material was added, and after standing one hour, with occasional stirring, the dyed fibre was collected on a Gooch filter, washed with water, dried, and weighed. In some cases the filtrate from the fibre was a deep green instead of the brownish-red colour of the ferric ferricyanide solution, and it happened in a number of cases that a loss of weight followed the treatment, showing that soluble products were formed by the action of the ferricyanide solution on some of the constituents of the cellulose.

The results of the first series of estimations are given in Table I. After weighing out the samples of the more resinous woods, they were extracted with ether before the alkaline boiling.

The results which are summarised in Table I. show that the chlorination method is not easily controlled for quantitative estimations. In estimations of this sort it is not to be expected that the results will be concordant to small fractions of a per cent, but the variations observed seem rather too large even for proximate analyses. As stated above, the difficulty of judging the end-point of the process was very great. The same treatment did not always yield the same kind of a product nor show the same percentage of cellulose. If the chlorinations were continued until a perfectly white product was obtained, the percentages were not always alike and seemed to be too low. The results of the ferricyanide reaction did not appear to be of much help.

To assist in clearing up some of these points, we have carried out a series of systematic determinations on four different kinds of wood. Of each kind of wood four (five in the case of No. 1) samples of about five grms. were taken. The first sample was boiled in alkaline solution as described above, chlorinated once for one hour, boiled in sulphite solution, treated with permanganate and sulphurous acid, washed, and dried; the next sample was treated in precisely the same way except that it had two one-hour chlorinations and the accompanying sulphite boilings; and so on, each sample receiving one more

chlorination than the one before it. In the case of Wood No. 1 the final washings were carried out in the funnel, as in the former experiments, with the other woods the final product was boiled for five minutes in a large volume of distilled water in order to ensure the removal of all reagents. The different kinds of wood, and each of the celluloses, were tested by the ferricyanide reaction. The results are summarised in Table II.

TABLE II.

		Colour.	Per cent of cellulose.	Per cent gain by ferricyanide reaction.
Wood No. 1: Heartwood of Red Spruce.				
Wood		—	—	13·85
Cellulose by chlorination	1	Light brown	61·9	2·52
,, ,,	2	Light cream	58·5	0·11
,, ,,	3	White	51·9	−1·50
,, ,,	4	White	49·1	−1·55
,, ,,	5	White	46·8	−1·42
Wood No. 2: Sapwood of Red Spruce.				
Wood		—	—	9·51
Cellulose by chlorination	1	Light brown	63·5	6·69
,, ,,	2	Light cream	53·5	0·79
,, ,,	3	White	51·3	−1·56
,, ,,	4	White	47·9	−2·83
Wood No. 3: Heartwood of Balsam Fir.				
Wood		—	—	11·63
Cellulose by chlorination	1	Light brown	57·3	4·2
,, ,,	2	Cream	49·4	2·54
,, ,,	3	White	44·1	2·02
,, ,,	4	White	44·6	1·75
Wood No. 4: Sapwood of Lodgepole Pine.				
Wood		—	—	7·77
Cellulose by chlorination	1	Dark cream	54·6	1·36
,, ,,	2	Light cream	54·3	1·40
,, ,,	3	White	52·3	0·87
,, ,,	4	White	49·1	−0·10

None of the woods here are very resistant, and in only one case, Balsam Fir, was trouble given by the presence of refractory particles which would not become perfectly white. In all cases when the fibre had received two chlorinations of one hour each, it bleached when again subjected to the action of chlorine gas, instead of turning to the orange-red characteristic of lignocelluloses. Cross and Bevan believe that this orange colour with chlorine is a *characteristic* reaction. If that be true, then the complete removal of the lignone complex must take place early during the third chlorination, and the percentage of cellulose falls in between the values found with two and with three chlorinations. The ferricyanide reaction fails to give wholly satisfactory results. We have never been able to obtain a cellulose from wood which does not give a blue-green colour with this reagent. Why the deep green filtrates should be obtained from some of the tests, and a loss of weight should occur, is not apparent.

The final working out of the following satisfactory analytical procedure was greatly aided by the realisation that the end-point was indicated by the bleaching of the cellulose in chlorine, and by finding that satisfactory samples could be secured by the use of a wood-worker's rasp.

By holding the wood to be sampled in a vice, and rasping lightly, a finely fibrous sample is readily obtained. The best samples are prepared from green wood; when dry wood is to be sampled, it should be soaked or boiled until thoroughly softened before being rasped. The material is brought to an air-dry condition, any large pieces which may perchance be present picked out with forceps, and the very fine particles removed by shaking the air-dry sample on cheese cloth or a very fine sieve. The resulting uniform material is then dried at 98—100°, and 5 grm. portions used for analysis.

The first chlorination should be for one hour; the length of subsequent chlorinations must be to some extent a matter of judgment. If the fibre takes on a very deep orange, showing that a large amount of the lignone is still present, the second chlorination should be for a half or even three-quarters of an hour; if lighter colours appear, the time should be shorter. The wood of deciduous trees gives a far paler orange colour with chlorine than that of the coniferous species, and more readily yields a pure cellulose.

The rate of chlorine flow influences the length of exposure required. This is brought out in analyses 1 to 4 in Table III. In analyses 1 and 2 the chlorine was passed in slowly, the first chlorination was not complete, and a second treatment was required. In analysis 3, the gas was passed in more rapidly, and when the fibre was exposed to chlorine the second time it bleached at once. The final result is not influenced, provided the fibre is removed immediately after bleaching occurs. If the cellulose is not removed from the action of chlorine as soon as bleached, it is attacked and a significant loss occurs, as shown in analysis No. 4. When bleaching occurs, the funnel should be transferred to the filter flask, the cellulose treated with water containing a little sodium bisulphite to act as an "anti-chlor," then thoroughly washed, transferred to a large size Gooch crucible, and finally washed in the crucible with alcohol and ether. The first part of the drying should be at a gentle heat, ending with a temperature of 98—100°.

Several analyses are given in Table III., all of them satisfactory, except No. 4, where the chlorine was allowed to act on the bleached cellulose.

TABLE III.

No.	Material.	Chlorinations.	Per cent of cellulose.
1.	White oak—Sapwood	1 hour, 20 minutes, and to bleach	55·90
2.	,, ,,	Do. Do.	56·34
3.	,, ,,	1 hour and to bleach	56·40
4.	,, ,,	Do. Do.	54·79
5.	Red cedar—Sapwood	1 hour, 30 minutes, and to bleach	42·04
6.	,, ,,	Do. Do.	41·51
7.	,, Heartwood	Do. Do.	42·52
8.	,, ,,	Do. Do.	43·00
9.	Red spruce—Heartwood	1 hour, 10 minutes, and to bleach	58·95
10.	,, ,,	Do. Do.	58·60
11.	Cherry—Sapwood	1 hour and to bleach	54·72
12.	,, ,,	Do. Do.	54·43

The final products were all pure white, and none of them gave the lignin reaction with phloroglucinol and hydrochloric acid.

In conclusion, we desire to acknowledge our indebtedness to Mr. D. C. Parmelee for valuable assistance given us in the analytical work.—*Journal of the American Chemical Society*, xxix., No. 7.

Lothar Meyer Memorial.—As lately announced by Sir William Ramsay, Professor Wislicenus (of Tübingen) is arranging the establishment of a memorial to the late Professor Lothar Meyer. The Treasurer of the Chemical Society is prepared to receive donations towards the fund, and contributors are therefore requested to forward their subscriptions to him, in envelopes endorsed "Lothar Meyer Memorial," at Burlington House, W.

POTASSIUM AMMONOZINCATE.

A Representative of a New Class of Compounds.

By EDWARD C. FRANKLIN.

Following the programme of developing the ammonia system of acids, bases, and salts inaugurated in the Stamford University laboratory, Mr. F. F. Fitzgerald (*J. Am. Chem. Soc.*, xxix., 656) has succeeded in preparing an ammonia analogue of the potassium zincate which is generally (Abegg's "Handb. Anorg. Chem." ii., 338) assumed to be formed when metallic zinc, zinc oxide, or zinc hydroxide is dissolved in an aqueous solution of potassium hydroxide. He obtained this ammono salt, to which he gave the formula $Zn(NHK)_2.2NH_3$, by the action of an ammonia solution of potassium amide on metallic zinc and on zinc amide in accordance with the equations $Zn + 2KNH_2 + Am = Zn(NHK)_2.2NH_3 + H_2$, $Zn(NH_2)_2 + 2KNH_2 = Zn(NHK)_2.2NH_3$, which are obviously analogous to the reactions whereby Comey and Jackson (*Am. Chem. Journ.*, xi., 145) prepared the compounds $Zn_3O_6Na_4H_2.19H_2O$ and $(ZnO_2NaH)_2.7H_2O$, and Förster and Gunther (*Zeit. Elektrochem.*, vi., 301) the compound to which they gave the formula $(OH)Zn(ONa).3H_2O$. (This latter compound, it should be noted, is probably identical with the compound $(ZnO_2NaH)_2.7H_2O$, of Comey and Jackson, inasmuch as the two products differ in composition by half a molecule of water only.)

Unfortunately Fitzgerald's work was brought to a sudden end by the great earthquake before entirely satisfactory evidence as to the composition of his product had been procured. In view of the importance of establishing definitely the existence of a compound belonging to this group of the ammonia system, the writer has continued Mr. Fitzgerald's work and has succeeded in preparing a beautifully crystallised compound, the analytical data for which point sharply to the formula $Zn(NHK)_2.2NH_3$, or $Zn(NH_2)_2.2KNH_2$, thus confirming the earlier results.

Preparation of Potassium Ammonozincate.

The pure compound has been prepared by the action of an excess of potassium amide in solution in liquid ammonia on pure, water-free, ammoniated zinc iodide in accordance with the equation $ZnI_2.4NH_3 + 4KNH_2 = Zn(NHK)_2.2NH_3 + 2KI + 2NH_3$. The manipulative details were carried out as follows, using the form of apparatus and methods of procedure previously described (*Journ. Am. Chem. Soc.*, xxvii., 830) by the writer. Clean metallic potassium, together with a few milligrms. of platinum black, were introduced into one leg of the apparatus, after which this leg was closed before the blowpipe. Into the other leg was then introduced the zinc salt, which was melted in a current of ammonia gas to a perfectly clear, colourless liquid, after which the tube was sealed as usual. As soon as the conversion of the metallic potassium into potassium amide was complete, the solution of the latter was poured in excess into the leg containing the zinc iodide. Zinc iodide is soluble as such to a limited extent only. Addition of a small quantity of potassium amide greatly increases the solubility of the zinc salt, a behaviour for which the explanation is not obvious. Increasing the amount of potassium amide finally produces a permanent flocculent precipitate which, in the presence of an excess of the precipitant, gradually, in the course of some hours, changes into a mass of dense, colourless, well formed crystals. After washing a few times the salt is obtained pure.

Method of Analysis.

For analysis the tube containing the pure salt was separated from the remainder of the apparatus and evacuated of its gaseous contents by means of a mercury pump at laboratory temperature. The tube was weighed, delivered of its contents, evacuated and weighed again, thus giving the weight of the salt which during this process has at no time been in contact with the air or other source of contamination with water. The substance in solution in dilute hydrochloric acid is divided into aliquot parts, in one of which the nitrogen is determined by distillation with potassium hydroxide and titration of the distillate after the usual volumetric method for ammonia. In another portion of the solution the zinc is precipitated by the addition, in excess, of a measured amount of a standard solution of sodium carbonate, followed by digestion on the water-bath until the ammonia is entirely removed and the precipitation of the zinc is complete. The filtrate from the zinc carbonate is acidified with hydrochloric acid, evaporated to dryness and ignited, thus giving a mixture of known sodium chloride content.

Analytical Data.

The following analytical results have been obtained:—

Preparation I. One-fourth of 0·5962 grm. of the substance gave 0·0398 grm. nitrogen; another fourth gave 0·0586 grm. zinc oxide.

Preparation II. One-half of 0·6858 grm. of this preparation gave 0·093c grm. nitrogen; the other half gave 0·1367 grm. zinc oxide and 0·2446 grm. potassium chloride.

Preparation III. One-half of 0·7424 grm. of the substance gave 0·1008 grm. nitrogen; one-fourth of 0·7424 grm. of the substance gave 0·0727 grm. zinc oxide and 0·1338 grm. potassium chloride.

From these results the following percentages of the respective constituents have been calculated:—

	Calculated for $Zn(NHK)_2.2NH_3$.	Found. I.	II.	III.
N	27·04	26·7	27·1	27·1
Zn	31·44	31·5	31·9	31·4
K	37·70	—	37·5	37·7

It should be mentioned here that the discrepancies in the analytical data obtained by Fitzgerald were undoubtedly caused by the presence of water, very small quantities of which, acting hydrolytically on the ammono salt, set free ammonia and form the hydroxides of zinc and potassium.

It is of further interest in this connection to note that the writer, in his attempts to prepare, filter, and wash this compound in a piece of apparatus devised for working with liquid ammonia solutions at atmospheric pressure, always obtained products which were low in ammonia and high in potassium and zinc, the results, as he believes, of his inability to exclude all traces of moisture when working with such a cold liquid as ammonia is at low pressures. The moisture probably finds its entrance past the numerous stoppers and stop-cocks used.

Properties of the Salt.

Potassium ammonozincate is but slightly soluble in liquid ammonia, but is dissolved energetically and with the evolution of much heat in dilute aqueous acids. It is also soluble in liquid ammonia solutions of ammonium salts. It is very susceptible to the action of water, which converts it into ammonia, zinc hydroxide, and potassium hydroxide; even very short exposure to the action of the moisture of the air produces a superficial, sticky layer on the clean, dry crystals. It is not explosive. When heated *in vacuo*, potassium ammonozincate remains unaffected up to about 160°. As the temperature is increased the substance melts and gives off ammonia. One specimen heated to 250° for some hours until the evolution of ammonia had practically ceased, gave off 11·3 per cent of ammonia and yielded a dark, varicoloured residue which gave on analysis 18·7 per cent nitrogen, 36·8 per cent zinc, and 44·7 per cent potassium. Another specimen heated to 300° for a considerable time lost 11·6 per cent ammonia and gave a residue containing 18·8 per cent nitrogen. The evolution of one and a-half molecules of ammonia from $Zn(NHK)_2.2NH_3$ would require a loss of 12·3 per

cent in weight, while a compound of the composition $Zn(NHK)_2.\frac{1}{2}NH_3$, would contain 19·2 per cent nitrogen, 35·8 per cent zinc, and 43·1 per cent potassium. As the temperature is raised ammonia mixed with permanent gases is given off, and at the same time rings of metallic potassium and zinc are deposited in the cooler end of the tube. When a third specimen was heated to 325° for many hours it lost 14·8 per cent of its weight, apparently showing that even at this temperature all the ammonia of crystallisation is not driven off. On emptying the tubes after heating these preparations to 250° and higher, the glass walls of the tubes were found to be much attacked by the melted salt, a fact which accounts for the divergent analytical results, and at the same time discouraged any further attempts to obtain a definite compound by the elimination of ammonia from the compound $Zn\,NHK)_2.2NH_3$. In one experiment a tube lined with platinum was used in the hope that definite results might thus be obtained, but it was found that the melted salt also attacked this metal. It should be pointed out, however, that the results obtained point to the probable existence of a compound of the formula $Zn(NHK)_2.\frac{1}{4}NH_3$.

Summary.

It is shown by the work described above that a potassium ammonozincate, an ammonia analogue of the hypothetical water salt, potassium zincate, is obtained in the form of a definite, well crystallised compound by the action of a liquid ammonia solution of potassium amide, first on metallic zinc, second on zinc amide, and third on zinc iodide, in accordance with the following respective equations:—

1. $Zn + 2KNH_2 + Am. = Zn(NHK)_2.2NH_3 + H_2$,
2. $Zn(NH_2)_2 + 2KNH_2 = Zn(NHK)_2.2NH_3$,
3. $ZnI_2.4NH_3 + 4KNH_2 = Zn(NHK)_2.2NH_3 + 2KI + Am.$

—*Journal of the American Chemical Society*, xxix., No. 9.

THE ACTION OF HYDROCHLORIC ACID ON MANGANESE DIOXIDE.

(Preliminary Paper).

By WILLIS B. HOLMES.

A great deal of work has been done upon the interaction of hydrochloric acid and manganese dioxide. Although the bulk of experimental evidence seems to point to the probable formation of the trichloride and tetrachloride of manganese, a final decision in this case has not yet been reached. None of the intermediate products of the reaction have ever been isolated, and the experimental work bearing upon this subject is of an indirect nature. Two general methods of attacking this problem have been in vogue; the treatment of manganese dioxide with an ethereal solution or with an aqueous solution of hydrogen chloride and the subsequent analyses of the solutions thus obtained. The former method excludes the presence of water, except such as is formed by the reaction itself, while the latter method introduces it.

Manganese Dioxide Treated with an Ethereal Solution of Hydrogen Chloride.—Nicklès (*Ann. Chem.*.. 4 , v., 161) treated manganese dioxide with an ethereal solution of hydrogen chloride, and obtained a dark green solution, the colour of which, on further dilution with ether, changed to a deep violet. On saturating this solution with hydrogen chloride he obtained a green oil which he claimed contained manganese tetrachloride. One analysis gave results for $MnCl_4.12(C_2H_5)_2O.2H_2O$. Nicklès' results, however, are not conclusive.

Christiansen (*Journ. Prakt. Chem.*, xxxiv., 41, and xxxv., 57) suspended manganese dioxide in ether, saturated the ether with chlorine, and obtained a violet solution. By decanting this violet solution, he obtained a black residue which also partly dissolved in ether and gave the same violet colour to the solution. (This black residue is of interest, as it probably contained some manganese trichloride). He then treated manganese dioxide with ether which had been saturated with hydrogen chloride, and obtained a green solution. He considered that the violet solution and the green solution both contained the same dissolved substance, the difference in colour being due to the presence of water in the former case. For analysis a portion of the green solution was run into a solution of potassium iodine and the liberated iodide titrated with a solution of sodium thiosulphate. From these results the available chlorine was estimated. (The term available chlorine refers to the chlorine in excess of that required for manganous chloride). The total manganese in this solution was then determined. The average ratio of total manganese to available chlorine from seven analyses was 1 : 1·06. He thus concluded that manganese trichloride was formed in both cases. By working at a temperature of about −10° he obtained a higher ratio—approximately, 1 : 1·5—and thought that the tetrachloride might be formed at lower temperatures.

Franke (*Journ. Prakt. Chem.*, xxxvi., 31 and 451) repeated Christiansen's work, and obtained the same ratio of manganese to available chlorine, approximately 1 : 1, but interpreted the results differently. He thought that hydrogen chloride, instead of water, caused the difference between the blue and green solutions; that the green solution with the excess of hydrogen chloride contained chloromanganic acid, while the violet solution contained manganese tetrachloride. Manganous chloride was always present as a decomposition product, and united with the chloromanganic acid forming manganous chloromanganate,

$$MnO_2 + 6HCl \rightarrow H_2MnCl_6 + 2H_2O,$$
$$MnCl_2 + H_2MnCl_6 \rightarrow MnMnCl_6 + 2HCl.$$

The green solution on further dilution with ether separated into manganous chloride and manganese tetrachloride, the violet colour becoming evident as the tetrachloride was extracted. The ratio 1 : 1 was thus interpreted. His analysis of the violet solution gave the ratio of total manganese to available chlorine from 1 : 1·68 to 1 : 2·35. This ratio indicated the presence of the tetrachloride. The violet solution treated with a little water gave a precipitate of hydrated manganese dioxide.

Manganese Dioxide Treated with an Aqueous Solution of Hydrogen Chloride.—Fisher (*Journ. Chem. Soc.*, xxxiii., 409) treated manganese dioxide with strong hydrochloric acid in the proportion of one part of the dioxide to ten parts of the acid. The resultant solution was filtered through spun glass and run into a burette. A known volume was then delivered into a solution of potassium iodide, and the iodine titrated in the usual way. An equal volume was then run into a solution of sodium acetate, and the precipitated manganese was separated, ignited, and weighed as mangano manganic oxide. The filtrate was then treated with potassium iodide, and the free chlorine estimated. This, subtracted from the result in the first solution, gave the available chlorine. The ratio of precipitated manganese to available chlorine was approximately 1 : 2, and hence the conclusion that the tetrachloride was formed. He assumed that the precipitated manganese was entirely a hydrated dioxide, and that the tetrachloride, in the presence of hydrochloric acid, existed in a form analogous to chloroplatinic acid.

Pickering (*Journ. Chem. Soc.*, xxxv., 654) repeated Fisher's work and obtained different results. His general method of procedure was the same, except that he used water instead of a solution of sodium acetate, and analysed his precipitated manganese by a method whereby he could estimate not only the total manganese, but also the amount of dioxide which it contained. His results showed that the precipitated manganese was not entirely a dioxide but a mixture of different oxides; that the ratio of total manganese to available chlorine was nearly 1 : 1·64, and that the ratio of manganese dioxide to available chlorine

was 1 : 2. He concluded that the reaction took place as follows :—

I. $2MnO_2 + 8HCl \rightarrow Mn_2Cl_6 + Cl + 4H_2O$,
II. $Mn_2Cl_6 + 2H_2O \rightarrow MnO_2 + MnCl_2 + 4HCl$,

because he was never able to obtain more than half of the manganese as a precipitate. If Equation II. was correct then the amount of precipitated manganese should increase if the experiment was performed in the presence of manganous chloride, whereas the amount should remain stationary if the tetrachloride was formed. The amount of precipitated manganese did increase when manganous chloride was added to the solution, which indicated the presence of the trichloride. The effect of temperature upon the amount of manganese precipitated also indicated the formation of the trichloride. If the substance was a tetrachloride, at low temperatures, 100 per cent should be precipitated, and in the case of the trichloride only 50 per cent. At 60°, less than 10 per cent was precipitated, and at low temperatures the amount approached 50 per cent.

Vernon studied the action of hydrochloric acid on manganese dioxide by estimating, at various temperatures, the rate of evolution of chlorine (*Phil. Mag.*, lxxxi., 469, and CHEMICAL NEWS, lxi., 203). If Pickering's view is correct,—

$$2MnO_2 + 8HCl \rightarrow Mn_2Cl_6 + Cl_2 + 4H_2O,$$

then half of the available chlorine ought to be evolved very rapidly. This was not found to be the case, especially at low temperatures. From the result of his experimental work, Vernon concluded that manganese tetrachloride is always the first product formed when manganese dioxide is dissolved in hydrochloric acid.

Wacher (*Chem. Zeitung.*, xxiv., 285) dissolved manganese dioxide in concentrated hydrochloric acid, and obtained a brown solution which, on dilution with water, gave a precipitate of hydrated manganese dioxide. He then passed chlorine into a solution of manganous chloride in concentrated hydrochloric acid, and obtained a similar brown solution. This solution also gave a precipitate of hydrated manganese dioxide when diluted with water. From these results he concluded that the tetrachloride of manganese was formed, but gave no experimental evidence to show that the precipitate was entirely hydrated manganese dioxide.

Double Salts.—Numerous double chlorides containing manganese trichloride and tetrachloride have been isolated. Rice (*Journ. Chem. Soc.*, lxxiii., 258) and Newman (*Monatsh.*, xv., 489) obtained the double chlorides, $2KCl.MnCl_3$ and $2NH_4.MnCl_3$. Meyer and Best (*Zeit. Anorg. Chem.*, xxii., 169) obtained similar double salts with quinoline and pyridine hydrochloride $MnCl_3.2C_9H_7NHCl$ and $MnCl_3.2C_5H_5NHCl$. They also obtained the double chlorides, $2CsCl.MnCl_3$, $MnCl_4.2KCl$, and $MnCl_4.MnCl_3.5KCl$. Reitzenstein obtained a dipyridine manganese tetrachloride (*Zeit. Anorg. Chem.*, xviii., 290).

Experimental Part.

Previous failures to isolate the intermediate products of the interaction of hydrochloric acid and manganese dioxide probably depend upon the fact that such products are decomposed by water and heat. The reaction itself liberates water, but it seemed possible by reducing the amount of water to a minimum and at the same time keeping the temperature low, to obtain some information concerning the nature of the products formed. This proved to be the case.

The method of treating manganese dioxide with a solution of hydrogen chloride in absolute ether was not found practical. While the ratio of precipitated manganese to available chlorine could be determined from such a solution, the total chlorine could not be estimated, as it was impossible to get rid of the excess of hydrogen chloride. Attempts to precipitate the product soluble in the ethereal solution by adding a large excess of carbon disulphide or toluene, proved unavailing. A green oily liquid could be obtained, but it was impossible to do anything with it. Some medium was then sought for which would not dissolve any of the compounds of manganese formed and at the same time would dissolve hydrogen chloride and not be affected by it, or by any of the decomposition products of the reaction. Carbon tetrachloride seemed to fulfil the necessary conditions, and was used throughout for the preparation of material.

The following method of procedure was followed. Five grms. of precipitated manganese dioxide was mixed with 200 cc. of carbon tetrachloride, and put in a long-necked 500 cc. vacuum flask. This flask was then inserted in a shaking machine. The shaking machine was made of a board 40 × 15 cm., with a hole in the middle for the insertion of the neck of the flask, and supported at each end by a 30 cm. upright. The neck of the flask was held in place by a perforated rubber stopper. A short shank extending from the side of the board was connected with an eccentric on wheel run by a small motor. This gave a lateral motion to the flask, which was inserted in a pneumatic trough filled with finely-ground ice and water. The shaking served the double purpose of keeping the flask and its contents cold and of agitating the mixture. Dry hydrogen chloride was then bubbled through the carbon tetrachloride. As water was formed during the reaction, no extreme precautions were taken to dry the gas, although it was passed through several towers filled with beads and sulphuric acid. Hydrogen chloride is not extremely soluble in carbon tetrachloride, so the gas was allowed to bubble through for an hour and a-half. The reaction was then practically complete, and the solid residue in the flask was separated by filtration.

The filtrate of carbon tetrachloride gave no test for manganese, but was coloured yellow from the dissolved chlorine. A large amount of chlorine was always formed, and could even be detected in the wash-bottle used to absorb the unused hydrogen chloride.

The solid residue consisted of a greenish black substance, which on standing slowly decomposed with the evolution of chlorine and hydrogen chloride. When it was dried in a desiccator with potassium hydroxide and sulphuric acid, decomposition set in, and a substance of a reddish brown colour remained; but when dried quickly by means of filter-paper and warmed, it gave off chlorine and hydrogen chloride. A little put in a large amount of water gave an immediate precipitate, probably hydrated manganese dioxide. Treated with absolute ether, it gave a solution of an intense violet colour. On standing, this solution gradually lost its violet colour, and manganous chloride separated out; but if kept cold the solution retained its colour from twelve to forty-eight hours. If hydrogen chloride was passed into this violet solution, it turned green. On continued washing of the original residue with ether the compound which imparted the violet colour was entirely dissolved out, and a reddish brown residue remained. This substance, which dissolved in ether with the formation of a violet solution, proved to be manganese trichloride.

The reddish brown residue was much more stable than the original residue. It could be kept in a desiccator for a long time without undergoing any appreciable decomposition, but decomposed immediately on exposure to moist air. When warmed it gave off chlorine, and left a residue of manganous chloride. It dissolved in absolute alcohol forming a solution of deep wine colour which slowly decolorised on standing. This substance proved to be manganese tetrachloride. About one-half of the original residue was manganese trichloride, the remainder being a mixture of manganous chloride and manganese tetrachloride.

Manganese Trichloride.—The analysis of this substance offered many difficulties. The solid could not be prepared in a condition pure enough for analysis. Attempts to obtain the trichloride from the ethereal solution by evaporating the ether by means of a current of dry cold air proved unavailing, as decomposition always set in. The analysis of the ethereal solution was then attempted. In preparing this solution for analysis the utmost care was

necessary. It was very difficult to remove the last traces of hydrogen chloride, and all reagents used had to be anhydrous and kept at a low temperature. The work had to be performed as expeditiously as possible, and a dilute solution used in order to prevent decomposition.

The residue of mixed chlorides from the flask was first washed with a large amount of carbon tetrachloride. This removed part of the hydrogen chloride. It was next washed with carbon disulphide to remove the carbon tetrachloride, and then transferred to a flask containing carbon disulphide, to which a little ether had been added, and shaken. This treatment seemed to be the most effective method of removing the last traces of the hydrogen chloride, and was repeated a second time. The residue was then transferred to a funnel and washed with ether, which had been cooled with solid carbon dioxide, until about two-thirds of the trichloride had been removed. The filter-paper and residue were then put in a special funnel connected with a litre filtering flask. The funnel was surrounded with a jacket so that it could be kept cold by means of ether and solid carbon dioxide. The flask held 250 cc. of ether, and was placed in a mixture of ice and salt. The residue was then washed with about 100 cc. of the cold ether, and this solution, diluted with the ether in the flask, was used for analysis.

In the analysis, three quantities were estimated; the available chlorine, the total chlorine, and the total manganese. In certain cases the precipitated manganese was also obtained. A 50 cc. pipette, protected by a drying tube, was used to run off equal portions of the solution into six receptacles. The first four consisted of litre filtering flasks fitted with rubber stoppers, and carrying glass tubes large enough for the insertion of the pipette. One and two each contained about 300 cc. of a dilute solution of potassium iodide, and were used to estimate the available chlorine. Three and four each contained about 300 cc. of a dilute solution of silver nitrate to which a little nitric acid had been added, and were used to estimate the total chlorine. The arms of the flask were connected with U-tubes containing the same solutions, and these in turn were connected with an aspirator. Air was aspirated through each flask during the filling. The contents of the tubes were afterwards added to the flasks. Five and six were beakers each containing about 200 cc. of water, and were used to determine the total manganese.

The iodine was titrated with a one-tenth normal solution of sodium thiosulphate, and from the results obtained the available chlorine was estimated. The silver chloride was determined by the regular crucible method, and the total chlorine estimated. Only a part of the manganese was precipitated, so ammonium hydroxide and bromine water were added to the solution to precipitate all the manganese. The precipitate was then filtered, washed, ignited in a Rose crucible, and weighed as mangano-manganic oxide. It was then converted into manganous sulphide, and weighed again. When the quantity of manganese was very small, the oxide and sulphide methods gave identical results, but with larger amounts there was a slight variation. The sulphide results were used throughout as being the more reliable.

Analysis I.—This analysis was a preliminary one performed to get some idea of the ratio between the available chlorine and the total chlorine. It gave results as follows:—

Available chlorine (grm.) ..	0·0198	0·0198
Total chlorine (grm.)	0·0618	—

Ratio of available chlorine to total chlorine, 1 : 3·12.

Analysis II.—This analysis was performed before it was realised that the manganese trichloride retained some hydrogen chloride. The results are inserted, however, as they give an indication of the amount of hydrogen chloride retained. The residue was only washed with enough carbon disulphide to insure the complete removal of the carbon tetrachloride, and the ethereal solution was then prepared. This washing removed some of the hydrogen chloride, but enough remained to give an indication of the probable amount retained. Two additional portions of the ethereal solution were run into two beakers, each containing 300 cc. of water, and the filtrates were examined as follows:—The first was tested for free chlorine with a negative result, and the second for manganese which had not been precipitated.

Available chlorine (grm.) ..	0·0212	0·0212
Total chlorine (grm.)	0·0758	0·0757
Total manganese (grm.) ..	0·0346	0·0343
Manganese in filtrate (grm)...	—	0·0168

0·0344 grm. of manganese requires 0·0665 grm. chlorine for the trichloride. Excess of chlorine 0·0093 grm., equivalent to 0·0096 grm. HCl. 0·1009 grm. $MnCl_3$ requires 0·0228 grm. HCl for the double chloride $MnCl_3HCl$. The above results suggest the double chloride $2MnCl_3.HCl$, but are indicative only and need further confirmation. The ratio of available chlorine to the calculated total chlorine is 1 : 3·13.

Analysis III.—The solution for this analysis was made with all possible precautions, but was a little too concentrated, and a slight decomposition was observed. Two additional portions of the ethereal solution were used to determine the ratio between the precipitated manganese and the manganese in the filtrate. These portions were each run into 500 cc. of water and immediately filtered.

Available chlorine (grm.) ..	0·0209	0·0209
Total chlorine (grm.)	0·0684	0·0684
Total manganese (grm.) ..	0·0348	0·0346
Precipitated manganese (grm.)	0·0167	0·0167
Manganese in filtrate (grm.)..	0·0183	0·0179

Theoretical ratio, $Mn\,Cl_3 = 0·517$. Found, 0·507.

0·0347 grm. of manganese should require 0·0671 grm. of chlorine for the trichloride.

Ratio of available chlorine to total chlorine, 1 : 327.

Ratio of precipitated manganese to manganese in the filtrate, 1 : 1·08.

Analysis IV.—This analysis was made to determine the ratio between the total manganese and the total chlorine. Precautions were taken to wash the residue very carefully, and use a very dilute solution to insure a minimum of decomposition.

Total chlorine (grm.)	0·0319	0·0320
Total manganese (grm.) ..	0·0164	0·0165

Theoretical ratio, $Mn\,Cl_3 = 0·517$. Found, 0·515.

Properties of the Trichloride.—Manganese trichloride is a solid almost black in colour, with a slight greenish tinge. Heat breaks it up, with the evolution of chlorine, and it is immediately decomposed by water. Absolute ether is the best solvent yet found for the trichloride. When allowed to stand in a desiccator it decomposes into manganous chloride and manganese tetrachloride. All samples thus treated gave the reddish-brown substance characteristic of the tetrachloride. The trichloride dissolves in absolute alcohol, giving a wine-coloured solution which answered all tests for the tetrachloride. A small amount of this wine-coloured solution, treated with a large amount of absolute ether and kept cold, soon assumed the violet colour characteristic of the trichloride. It is thus possible to pass from one chloride to the other and back again. This, together with the fact that only half of the manganese is precipitated when the ethereal solution is run into water, indicates that the breaking down of the trichloride takes place in two stages, as Pickering observed (*Journ. Chem. Soc.*, xxxv., 654).

I. $Mn_2Cl_6 \rightarrow MnCl_2 + MnCl_4$.

II. $MnCl_4 + 2H_2O \rightarrow MnO_2 + 4HCl$.

The composition of the precipitate has not yet been determined. This will be done, however, when the quantitative study of this reaction is taken up.

Manganese Tetrachloride.—The tetrachloride was prepared by treating manganese dioxide, suspended in carbon tetrachloride, with hydrogen chloride. The same method of procedure as was used in preparing the trichloride was followed, and the same precautions observed. The residue

was washed with absolute ether to remove the trichloride. Persistent washing with ether failed to remove the last traces of the trichloride, so the residue was dried by means of filter-paper and put in a desiccator to allow the remaining trichloride to decompose. This failure to remove the last traces of the trichloride was probably due to the slight decomposition of the tetrachloride when some halogen absorbent was present. Samples of the tetrachloride when first suspended in ether gave no coloration, but the ether soon assumed the violet colour of the trichloride. Attempts to prepare pure manganese tetrachloride by the above method proved unavailing, as manganous chloride was always formed. Absolute alcohol was the only solvent found in which the tetrachloride was soluble, and such a solution was analysed. Manganese chloride is soluble in absolute alcohol, so the amount present had also to be determined.

The solution for analysis was prepared in the following way :—The residue, after standing in the desiccator, was transferred to the funnel of the special filtering flask previously described. The funnel was kept cold by means of ether and solid carbon dioxide. The flask held 250 cc. of absolute alcohol, and was surrounded with a mixture of ice and salt. About 100 cc. of absolute alcohol, which had been cooled with solid carbon dioxide, was then filtered through this funnel. Four portions of the resultant solution were then pipetted off and run into the same flasks as were used with the trichloride for the estimation of available and total chlorine. Two additional portions were run into two beakers, each holding 500 cc. of water, and the precipitated manganese then determined. This result gave the amount of manganese contained in the tetrachloride. The filtrate contained manganous chloride, and this manganese was then precipitated and estimated. The sum of the two gave the total manganese. In the analysis one precaution had to be observed. The precipitated manganese dioxide and alcohol interact unless the precipitation is made in a large volume of water and the filtration performed immediately.

Analysis I.—In this analysis the manganese was precipitated in 300 cc. of water, and the filtration was delayed for a short time. The results, consequently, are a little irregular.

Analysis II.—In this analysis the manganese was precipitated in 500 cc. of water and the filtration performed immediately.

Properties of the Tetrachloride.—This chloride is a solid of reddish brown colour, stable at ordinary temperature, if kept dry, but it quickly decomposes on exposure to moist air. Samples have been kept for several weeks in a desiccator without undergoing appreciable decomposition. But in a large amount of water the tetrachloride gives an immediate precipitate, probably hydrated manganese dioxide. Heated to 100° it gives off chlorine, and a residue of manganous chloride remains. When the tetrachloride is suspended in ether and kept cold it slowly decomposes into the trichloride, imparting the characteristic violet colour to the solution. If an excess of alcohol is added to this solution, some tetrachloride is again formed. Suspended in ether with mercurous chloride it decomposes more rapidly, but all the ordinary reducing agents such as can be used in a solution nearly anhydrous cause immediate decomposition without the intermediate stage. Absolute alcohol seems to be the only solvent which will dissolve the tetrachloride without rapid decomposition. If the alcohol contains a little water the solution is decolorised more quickly.

Summary.

1. When manganese dioxide, suspended in carbon tetrachloride, is acted upon by hydrogen chloride, manganese trichloride and manganese tetrachloride are formed.

2. Manganese trichloride has been isolated and its properties described.

3. When an ethereal solution of manganese trichloride s mixed with a large volume of water only half of the manganese is precipitated.

Analysis I.	Found (grm.).	Calc. (grm.).
Available chlorine	0·0192	—
	0·0192	—
Total chlorine	0·0872	0·0874
	0·0874	0·0850
Chlorine in $MnCl_4$	—	0·0428
	—	0·0389
Chlorine in $MnCl_2$	—	0·0446
	—	0·0461
Precipitated manganese ..	0·0164	—
	0·0151	—
Manganese in $MnCl_2$.. ..	0·0346	—
	0·0358	—
Total manganese	0·0510	—
	0·0509	—

$$\frac{\text{Available chlorine}}{\text{Total chlorine}} = \frac{0\cdot0192}{0\cdot0408} = 0\cdot470.$$

$$\frac{\text{Precipitated manganese}}{\text{Chlorine in } MnCl_4} = \frac{0\cdot0157}{0\cdot0408} = 0\cdot385. \quad \text{Theory, } 0\cdot387.$$

Analysis II.	Found (grm.).	Calc. (grm.)
Available chlorine	0·0059	—
	0·0060	—
Total chlorine	0·0442	0·0440
	0·0442	0·0443
Chlorine in $MnCl_4$	—	0·0140
	—	0·0140
Chlorine in $MnCl_2$	—	0·0300
	—	0·0303
Precipitated manganese ..	0·0054	—
	0·0054	—
Manganese in $MnCl_2$.. ..	0·0233	—
	0·0235	—
Total manganese	0·0287	—
	0·0289	—

$$\frac{\text{Available chlorine}}{\text{Total chlorine}} = \frac{0\cdot0060}{0\cdot0140} = 0\cdot429.$$

$$\frac{\text{Precipitated manganese}}{\text{Chlorine in } MnCl_4} = \frac{0\cdot0054}{0\cdot0140} = 0\cdot386. \quad \text{Theory, } 0\cdot387.$$

4. Manganese tetrachloride has been isolated and its properties described.

5. When an alcoholic solution of manganese tetrachloride is diluted with a large volume of water, all the manganese is precipitated.

6. Manganese tetrachloride is probably the first product formed when manganese dioxide and hydrochloric acid interact.—*Journal of the American Chemical Society*, xxix., No. 9.

OBITUARY.

LORD KELVIN.

With deep regret we chronicle the death, on the 17th inst., of the Right Honourable William Thomson, Baron Kelvin, the last survivor of that band of intellectual giants—Faraday, Darwin, Clerk Maxwell, Joule, Huxley, Lyell—whose achievements shed such glory on the mid-Victorian era.

In the shadow of a great loss it is hard to write dispassionately, but we do not hesitate to say that no man has done more than Lord Kelvin to mould the destinies of his country in those scientific directions which constitute true progress. If we seek to trace out the material steps which during the last half century have placed British science in the first rank, we shall come, in most cases, to a substratum based on and due to an observation of Lord Kelvin's. Few men of his generation have given to the world more discoveries which have ramified in so many directions, or have done so much to advance human welfare.

Lord Kelvin's funeral took place on Monday in Westminster Abbey, in the presence of men of science from all parts of the United Kingdom and the Continent. He was followed to the grave by a numerous company of friends and pupils, where he rests at the feet of his great prototype Newton.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5th, 1907.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

The President announced that Professor Wislicenus, of Tübingen, was arranging to establish a memorial to the late Professor Lothar Meyer.

Certificates were read for the first time in favour of Messrs. Edward Philip Andreae, Ph.D., Crestalba, Champion Hill, S.E.; Marie Joseph Arsène Braun, Ph.D., 5, Aspinall Road, Brockley, S.E.; William Henry Collier, 13, Powis Gardens, Bayswater, W.; John Maxwell Heron, North House, Manningtree, Essex; Thomas Percy Hilditch, 4, Park Hall Place, E. Finchley, N.; Capet Darcy Morewood, Ferndale, Frodingham, Doncaster; Alfred William Oke, B.A., LL.M., 32, Denmark Villas, Hove; Douglas Robert Pinnoik, 31, The Gardens, E. Dulwich, S.E.; Arthur Robert Runeckles, 68, Kyrle Road, New Wandsworth, S.W.; Adolph Octavius Trechmann, The Old Palace, Rochester; Alfred Wade, Government Pharmacist, Fiji; Herbert Edmeston Watson, B.Sc., Tringhurst, Cranes Park, Surbiton; Harry Percy Wilson, 3, Audley Road, Colchester.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Arthur John Banks; Edward De Barry Barnett; John Forbes Bell; Frank Buckney, B.A.; Thomas Callan, B.Sc.; Frederic William Caton, B.A., B.Sc.; George Hugh Crisp, B.A.; Edward Henry Croghan; Edward Joseph Day, M.D., M.R.C.S.; Frederick Harold Dupré; Percy Vivian Dupré; Francis Bridger Dutton; Claude Scott Fawcitt; Charles Thomas Foreman; Thomas Rigby Greenough, B.A.; William Hay; William Doge Hutchinson, B.A.; Harry Ingham, M.Sc.; Benjamin Owen Jones; John Kaye, M.A., B.Sc.; Herbert Marsden, B.Sc.; Hubert Frederick Sankey Marshall; Gerald Hargrave Martin; John Edward Langford Moore; Charles Samuel Mummery; George Joseph Saunders, B.E.; William Bush Schober, A.M., B.Sc., Ph.D.; Robert Harry Smith; Harold Ramsay Stobie; Frederick Thomas, B.Sc.; Harold Munkman Timpany, M.Sc.; George Arthur Watson; Marcus Wechsler, D.Sc.; Edward Wheeler; Robert Whymper; Percy Williams, B.Sc.; David Willott, B.Sc.; William John Wilson; Hubert Arthur Wootton, B.A., B.Sc.

Of the following papers, those marked * were read:—

*239. "*The Affinity Constants of Bases as Determined by the Aid of Methyl-orange.*" (Preliminary Note.) By Victor Herbert Veley.

In a former communication (*Trans.*, 1907, xci., 155), it was shown that if x be the units of 0·1 cc. hydrochloric acid added to an $N/40{,}000$ solution of methyl-orange, and y be the heights of a variable tintometer column, expressed in centimetres, required to produce the required match in tint, then $y = kx - b$. In this expression, k is the essential factor (or constant) of y in terms of x and b is accidental.

Certain values of k were obtained for hydrochloric acid, as also for the hydrochlorides of some aminocarboxylic acids.

As it was thought that such values might serve to determine the amount of free hydrochloric acid, and hence the degree of hydrolysis of the hydrochlorides of bases, preliminary experiments were made without any special care with a sample of *m*-phenylenediamine hydrochloride. It was then found with aqueous solutions of this salt containing an equi-acidic quantity of this acid, whether free or combined, that the ratio $k[\frac{1}{2}C_6H_4(NH_2)_2,2HCl]/k\ HCl = 0{\cdot}5$ approximately. In other words, 50 per cent of the salt is hydrolysed into the free base and acid. As the result is identical with that obtained by Bredig (*Zeit. Phys. Chem.*, 1894, xiii., 214), it was thought that this very simple line of investigation might be pursued further. So far, the hydrochlorides of about forty bases of various degree of complexity, ranging from hydroxylamine to cinchonidine, have been examined. Several results are found to be in accordance with the expression of Arrhenius $k_0/k_w = (1-x)v/x^2$ (*Zeit. Phys. Chem.*, 1888, v., 17), even at the great dilutions examined, whilst in the case of bases of analogous composition the ratio of the hydrolysis values found is nearly equal to the ratio of the heats of neutralisation with hydrochloric acid.

*240. "*The Constituents of the Essential Oil of Nutmeg.*" By Frederick Belding Power and Arthur Henry Salway.

The material employed in this investigation consisted of an oil which was distilled from unlimed Ceylon nutmegs of good quality, and was obtained in a yield of 6·94 per cent. It had $d\ 15°/15° = 0{\cdot}8690$; $\alpha_D + 38\ 4'$ in a 1-dcm. tube; acid value, 0·81; ester value, 3·15. The more complete examination of the oxygenated constituents of the oil was accomplished by means of a product, designated heavy oil of nutmeg, from which the terpenes had been to a large extent removed. This had $d\ 20°/20° = 1{\cdot}102$; $\alpha_D + 1°\ 17'$ in a 1-dcm. tube; saponification value, 6·10.

This investigation has shown that the essential oil of nutmeg contains the following substances:—(1) eugenol and (2) *iso*eugenol (about 0·2 per cent); (3) *d*-pinene and (4) *d*-camphene (about 80 per cent); (5) dipentene (about 8 per cent); (6) *d*-linalool, (7) *d*-borneol, (8) *i*-terpineol, and (9) geraniol (about 6 per cent); (10) a new *alcohol*, yielding on oxidation a *diketone*, $C_8H_{14}O_2$ (a very small amount); (11) a trace of an *aldehyde* resembling citral, but yielding a *β-naphthacinchoninic acid* derivative melting at 248°; (12) safrole (about 0·6 per cent); (13) myristicin, $C_{11}H_{12}O_3$ (about 4 per cent); (14) myristic acid, in a free state (about 0·3 per cent), and apparently a small amount in the form of esters; (15) formic, acetic, butyric, and octoic acids, and a new *monocarboxylic acid*, $C_{13}H_{18}O_3$, all in the form of esters, and in relatively small amount.

This investigation has also shown that the portion of nutmeg oil which has hitherto been designated "myristicol" is a mixture of alcohols, of which terpineol appears to be the predominating constituent.

Discussion.

Dr. Wade remarked that none of the constituents which had been isolated seemed to possess the characteristic odour of nutmeg, and asked whether the authors had been able to trace this odour to its source.

Dr. Power stated that the characteristic odour of nutmeg oil is not that of any individual substance, but is due to the mixture of odorous compounds contained in the oil.

*241. "*The Resolution of* sec.*-Octyl Alcohol (Methylhexylcarbinol Octane-2-ol).*" By Robert Howson Pickard and Joseph Kenyon.

sec.-Octyl alcohol is readily converted into the acid phthalic ester. The dextro-sec.-*octyl hydrogen phthalate* is then obtained by the fractional crystallisation of its *brucine* salt from acetone, and the corresponding *lævo*-compound by the fractional crystallisation of the *cinchonidine* salt from aqueous acetone.

The *sec.*-octyl hydrogen phthalates have $[\alpha]_D\ 48{\cdot}2°$ in ethyl-alcoholic solution, and when hydrolysed yield the pure alcohols which have $[\alpha]_D\ 17°\ 9{\cdot}8'$.

242. "*The Velocity of Reduction of the Oxides of Lead, Cadmium, and Bismuth by Carbon Monoxide, and the Existence of the Suboxides of these Metals.*" By Francis Joseph Brislee.

The production of lead, cadmium, and bismuth suboxides by the reduction of the higher oxides with carbon monoxide has been investigated. The velocity of reduction of the oxides was determined by heating the oxides, contained in a porcelain boat, to 300° in an apparatus in which carbon monoxide was circulated. The boat was withdrawn from

time to time and the loss in weight observed. The time interval varied from one and a-half to six hours. The results were then plotted as time-reduction curves, and these showed a distinct break at the point at which the analytical composition of the product was near that required for the suboxide. The position of the break was not always at the suboxide point, the position depending on the relative velocities of the two reductions, namely :—

1. Oxide → suboxide.
2. Suboxide → metal.

When the velocity of 1 is very different from 2, then the break will occur at the point when the oxide is entirely reduced to suboxide. When these two velocities are not very different, the first stage of the reduction is—

(1*a*) Oxide → suboxide → metal,

and the second is—

(2*a*) Suboxide → metal,

and then the break will occur below the point, corresponding to complete reduction of the oxide to suboxide. The experiments made on the velocity of reduction of the oxides of lead, cadmium, and bismuth confirm Tanatar's results (*Zeit. Anorg. Chem.*, 1901, xxvii., 304) that the suboxides of these metals are definite chemical compounds, but do not prove the stability of these compounds. The suboxides of lead, cadmium, and bismuth are formed as intermediate phases in the reduction of the oxide to metal by carbon monoxide.

243. "*The Relation between Unsaturation and Optical Activity.* Part I. *The Menthyl and Bornyl Esters of β-Phenylpropionic, Cinnamic, and Phenylpropiolic Acids.*" By THOMAS PERCY HILDITCH.

In order to throw further light on Walden's statement that increase of unsaturation in a compound is accompanied by increase in rotatory power, the author has prepared and investigated the properties of the menthyl and bornyl esters of the above three acids. Menthyl hydrocinnamate (m. p. 28°), menthyl phenylpropiolate (m. p. 33°), and bornyl phenylpropiolate (m. p. 45°) were obtained as nearly colourless, crystalline solids, whilst the other three esters were found to be liquid at the ordinary temperature. The boiling-points of the compounds, as well as the specific gravities, seems to show a regular increase with increase of unsaturation, whilst the refractive indices rise with a change to an ethylenic linking, but fall to an intermediate value for the further change to an acetylenic compound.

The following conclusions were arrived at as regards optical activity :—

1. The change in rotation for either change of constitution is relatively small.

2. The changes are nevertheless perfectly definite, and occur in a regular manner for corresponding stages of unsaturation (the rotations being measured at three successive concentrations in each of two solvents, chloroform and acetone).

3. The conversion of a saturated to an ethylenic bond is accompanied by an increase in optical activity, whilst the change from a saturated to an acetylenic linking produces a decrease in rotatory power.

4. In the case of esters, the change in rotation must be measured with reference to the difference between the specific rotation of the ester and that of the active alcohol from which it was formed.

5. Walden's results are confirmed so far as the change to an ethylenic linking is concerned, but there is a discrepancy with regard to the influence of the triple bond on the optical activity.

244. "*Methyl Ethers of some Hydroxyanthraquinones.*" By ARTHUR GEORGE PERKIN.

The author has re-examined the principal non-tinctorial derivatives of anthraquinone present in Chay-root, *Oldenlandia umbellata* (Perkin and Hummel, *Trans.*, 1893, lxiii., 1160, and 1895, lxvii., 817), and finds, contrary to the suggestion of Bock (*Monatsh.*, 1902, xxiii., 1008), that these compounds possess the constitution previously assigned to them, and do not contain reduced anthraquinone nuclei. The anthragallol dimethyl ether (A), m. p. 209°, when treated with alcoholic potassium acetate, gives the salt, $C_{16}H_{11}O_5K$, in violet-coloured leaflets, and on methylation forms *anthragallol trimethyl ether*, which crystallises in pale yellow needles, m. p. 167—168°. Anthragallol dimethyl ether (B) on methylation gives the same trimethyl ether, but the melting-points of this dimethyl ether and its acetyl derivative, previously given as 225—227° and 175° respectively, are now found to be 230—232° and 176—178°. Experiments indicate that, whereas in the compound (A) the methoxy-groups are present in the positions 1 : 3, in (B) they occupy the positions 1 : 2. Alizarin *a*-methyl, ether, m. p. 177—179°, on methylation gives alizarin dimethyl ether, m. p. 210—211°, and its acetyl compound, m. p. 212°, contains only one acetyl group. With potassium acetate, it gives a potassium salt, which forms garnet-red prismatic needles.

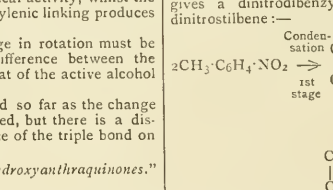
Hystazarin monomethyl ether on methylation gives *hystazarin dimethyl ether*, yellow needles, m. p. 235—236°, identical with the compound prepared from hystazarin itself. Finally, the natural *m*-hydroxyanthraquinone gave the methyl ether m. p. 192—193°. The so-called anthragallol dimethyl ether (C) was previously isolated in so small an amount that it could not be profitably re-examined, but, as the description of Bock's dimethyl ether (*loc. cit.*), does not agree with that assigned to this compound, it is possibly not a distinct substance.

A re-examination of emodin monomethyl ether (Perkin and Hummel, *Trans.*, 1894, lxv., 923) has confirmed the properties, melting-point, &c., previously assigned to it, so that Oesterle's conjecture that it is identical with his trihydroxymethylanthraquinone monomethyl ether (*Arch. Pharm.*, 1907, ccxlv., 287) is incorrect.

245. "*The Colouring Matters of the Stilbene Group.* Part IV. *Action of Caustic Alkalis on Para-nitrotoluene and its Derivatives.*" By ARTHUR GEORGE GREEN, ARTHUR HUGH DAVIES, and RONALD SMITH HORSFALL.

The authors find that the product of oxidation of substituted *p*-nitrotoluenes under the influence of caustic alkalis is largely dependent on the reactivity of the particular compound employed, this being determined by the nature of the ortho-substituent. Thus, whilst the cyano-derivative (like the chloro-derivative and the phenyl sulphonate already investigated) gave only a stilbene derivative, dibenzyl compounds were obtained from the methyl, methoxy-, and carboxy-derivatives, and both stilbene and dibenzyl derivatives from *p*-nitrotoluene itself. Those derivatives which react least easily with production of red condensation products yield dibenzyl compounds by preference, whilst those which react most readily and form violet to blue condensation products give chiefly stilbene compounds.

The results point to the conclusion that the condensation in question occurs in two stages, which may be more or less concurrent according to the degree of reactivity of the substance. The product of the first stage, when oxidised, gives a dinitrodibenzyl, that of the second stage a dinitrostilbene :—



Substituents which increase the reactivity of the substance therefore favour the formation of stilbene compounds.

A comparison of the relative reactivity of a number of such compounds under like conditions shows that, whilst the methyl, methoxy-, amino-, and carboxy-groups have

but little influence on the reactivity, the more strongly electro-negative groups, such as the sulphophenyl, cyano-, and nitro-groups, exert a powerful effect, that of the nitro-group being the strongest.

246. "*The Replacement of Alkyl Radicles by Methyl in Substituted Ammonium Compounds.*" By Humphrey Owen Jones and John Robertshaw Hill.

It has been shown previously (*Proc.*, 1901, xvii., 205; *Trans.*, 1905, lxxxvii., 1726) that the allyl and benzyl groups are readily displaced from amines or quaternary ammonium compounds by the methyl group on treatment with methyl iodide either at the ordinary temperature or at 100°.

The authors now find that the other alkyl groups, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, and *iso*amyl, are all replaced by methyl, sometimes in the cold, but more easily on heating with methyl iodide.

The two series of ammonium compounds derived from dimethylaniline and *p*-bromodimethylaniline (Hill, *Proc. Camb. Phil. Soc.*, 1907, xiv., 166) have been examined, and the phenyltrimethyl compound is the final product in each case. The replacement is due to the dissociation of the ammonium salt, in methyl iodide solution, into tertiary amine and alkyl iodide, the tertiary amine then combines with methyl iodide to produce the trimethyl compound, which is, in each case, much the least soluble of all. The ease with which the different groups are replaced varies considerably, and is dependent jointly on the extent to which the dissociation takes place and on the solubility of the ammonium salt. The ethyl or *iso*butyl group is most readily replaced, and the *iso*amyl group is the most difficult to displace.

247. "*Note on the Formation of Abnormal Platinichlorides.*" (A Correction). By Albert Ernest Dunstan.

In a recent communication (Dunstan and Cleaverley, (*Trans.*, 1907, xci., 1619), the preparation of three platinichlorides of the general formula B_4,H_2PtCl_6 was described. These were thought to belong to a new type of platinichlorides, but this is now found to be a mistake, as Werner (*Ber.*, 1903, xxxvi., 147) had collected all instances of such abnormalities known up to that date. Subsequently, Morgan and Micklethwait (*Trans.*, 1906, lxxxix., 863) added the cases of coumarin platinichloride and aurichloride, whilst Pickard and Kenyon have described (*Trans.*, 1906, lxxxix., 268) triethyl-, tripropyl-, and tribenzylphosphine oxide hydrogen platinichlorides, the latter of which had been prepared by Fleissner (*Ber.*, 1880, xiii., 1665), and by Letts and Collie (*Trans. Roy. Soc. Edin.*, 1888, xxx., I., 181).

248. "*The Nitrates of Dimethyl- and Methylethyl-thetine Menthyl Esters.*" By Samuel Smiles.

The nitrates of dimethyl- and methylethyl-thetine menthyl esters were prepared by precipitating concentrated aqueous solutions of the bromides with aqueous ammonium nitrate. *Dimethylthetine l-menthyl ester nitrate* forms colourless prisms which melt at 125—127°, and are very sparingly soluble in cold water or ethyl acetate, but readily so in the hot media. In alcoholic solution (1) 2 per cent the salt has $[\alpha]_D - 53{\cdot}9°$ and $[M]_D - 173°$ approximately. *Methylethyl-d-l-thetine l-menthyl ester nitrate* has $[M]_D$ about $-178°$ in the same solvent; it melts at 120—122°, and is slightly more soluble than the dimethyl derivative.

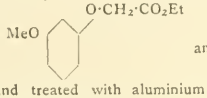
The methylethyl salt was fractionally crystallised from ethyl acetate with a view to resolving the thetine into optical isomerides. The experiments have been hitherto unsuccessful, probably owing to the instability of the ester to which attention has already been drawn (*Trans.*, 1905, lxxxvii., 451). The less soluble fraction contained the dimethylthetine ester, indicating the decomposition of the salt. The rotatory powers of the plantinichlorides of the dimethyl and methylethyl derivatives are corrected from these already given to $[M]_D - 438°$ for the dimethyl and $[M]_D - 380°$ approximately for the methylethylthetine, that for the diethyl being, as before, $[M]_D - 330°$.

249. "*Synthesis of Brazilinic Acid and the Lactones of Dihydrobrazilinic and Dihydrohæmatoxylinic Acids.*" (Preliminary Note). By William Henry Perkin, jun., and Robert Robinson.

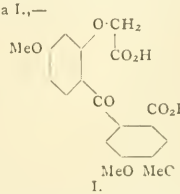
Brazilinic acid is formed when trimethylbrazilin is oxidised by permanganate (*Trans.*, 1902, lxxxi., 1030), $C_{19}H_{20}O_5 + O_5 = C_{19}H_{18}O_9 + H_2O$, and, on reduction, is converted into the lactone of dihydrobrazilinic acid, $C_{19}H_{18}O_9 + 2H = C_{19}H_{18}O_8 + H_2O$.

Since these two acids contain the same number of carbon atoms as trimethylbrazilin, it seemed probable that the determination of their constitutions might yield information which would definitely prove the constitution of brazilin. The authors have succeeded in synthesising brazilinic acid, the lactone of dihydrobrazilinic acid, and also the corresponding lactone of dihydrohæmatoxylinic acid by methods which leave no doubt as to their constitutions.

Brazilinic acid (m. p. 208°) is obtained in small quantity when a mixture of *m*-methoxyphenoxyacetic ester and *m*-hemipinic anhydride, is dissolved in carbon disulphide

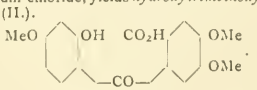


and treated with aluminium chloride. This synthesis clearly indicated that brazilinic acid must be represented by the Formula I.,—



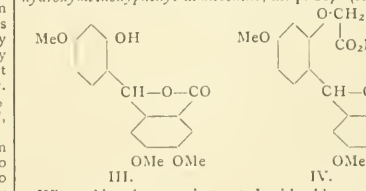
I.

and further proof of this was obtained by the synthesis of the *lactone* of *dihydrobrazilinic acid*, which was accomplished in the following way:—A mixture of resorcinol dimethylether and *m*-hemipinic anhydride, when treated with aluminium chloride, yields *hydroxytrimethoxybenzoylbenzoic acid* (II.).



II.

Reduction with sodium amalgam converts this acid into *hydroxymethoxyphenyl-m-meconine*, m. p. 207° (III.).

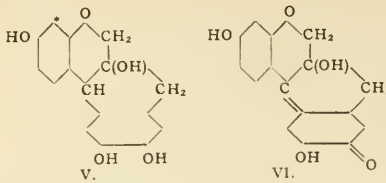


III. IV.

When this substance is treated with chloroacetic acid and potassium hydroxide, it is converted into an acid which melts at 226—227°, and is identical with the *lactone* of *dihydrobrazilinic acid*.

The latter acid must therefore have the constitution IV.

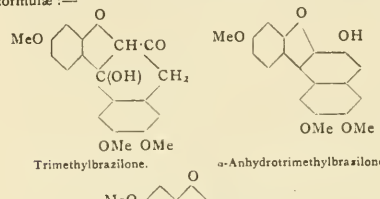
This synthesis not only confirms the constitution given above to brazilinic acid, but the authors consider that it proves clearly that brazilin must be represented by the constitutional formula V., first suggested by Werner and Pfeiffer (*Chem. Zeit.*, 1904, iii., 421).



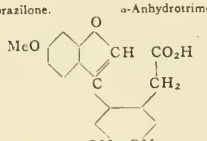
V. VI.

The *lactone* of *dihydrohæmatoxylinic acid* (m. p. 192°) was similarly synthesised from pyrogallol trimethyl ether and *m*-hemipinic anhydride by treatment with aluminium chloride and subsequent reduction and treatment with potassium hydroxide and chloroacetic acid. The constitution for hæmatoxylin is therefore derived from the above formula for brazilin by the introduction of a hydroxy-group at the point indicated by the asterisk.

An entirely different series of experiments on brazilein, carried out in conjunction with Paul Engels, has shown that the constitution of this important substance is represented by VI., an expression easily derived from the formula of brazilin given above. In the detailed account of the authors' experiments, it will be further shown that the important derivatives of trimethylbrazilin, namely, trimethylbrazilone, *α*-anhydrotrimethylbrazilone, and *ψ*-trimethylbrazilone, have constitutions represented by the formulæ :—



Trimethylbrazilone. α-Anhydrotrimethylbrazilone.



ψ-Trimethylbrazilone.

250. "*Condensations of Ketones containing the Group* ·CH_2·CO·CH· *with Esters in presence of Sodium Ethoxide*." By REGINALD WILLIAM LANE CLARKE, ARTHUR LAPWORTH, and ELKAN WECHSLER.

It has already been shown (*Trans.*, 1907, xci., 1919) that when cyanodihydrocarvone, which contains the above grouping, is acted on by nitrous esters in presence of sodium ethoxide, the attack occurs at the ·CH· group. It is now proved that menthone reacts in the same way, although when alkyl formates are used under analogous conditions it is the ·CH_2· group which is reactive. Pulegone appears first to be converted into *iso*pulegone, which then behaves like menthone, yielding a *hydroximino-acid* having the structure :—

$$CH_3 \geqq C \cdot C(:NOH) \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CO_2H.$$
$$CH_2$$

Bromocamphor yields only *iso*nitrosocamphor, and fenchone, in accordance with Semmler's view of its constitution, is quite unaffected.

The fact that esters of different kinds, acting under the influence of sodium ethoxide and similar agents, appear to select different points for attack on ketones containing the group ·CH_2·CO·CH:, is shown to be of considerable importance in connection with the question of the mechanism of syntheses brought about by such agents.

251. "*Acylogens and Thiocarbamides*." By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

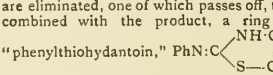
Following up their previous inquiries in the above direction (*Trans.*, 1907, xci., 912; compare also Dixon and Hawthorne, *Ibid.*, 122), the authors have now studied the behaviour of certain acyl chlorides with allyl-substituted thiocarbamides, and of phenylthiocarbamide with halogenised acyl halides.

Acetyl chloride unites with allylthiocarbamide to form C_3H_5·NH·C(NH)·SAc,HCl, white crystals, melting at 103—104°. On withdrawal of the combined halogen acid by weak alkali, the acetyl group migrates with production of C_3H_5·NAc·CS·NH_2, m. p. 96°, the latter, when melted, undergoing further change into C_3H_5·NH·CS·NHAc, m. p. 74°; of these three isomeric forms, the first alone is basic.

With *ab*-phenylallylthiocarbamide, acetyl chloride yields N-phenylpropylene-*ψ*-thiourea (Prager, *Ber.*, 1889, xxii., 2992).

Methyl chlorocarbonate gives with *ab*-phenylallylthiocarbamide the compound C_3H_5·NH·C(NPh)·S·CO_2Me,HCl (m. p. 87°); from this, water eliminates the halogen acid, and the carboxymethyl group thereupon migrates to form C_3H_5·N(CO_2Me)·CS·NHPh, m. p. 83°. Ethyl chlorocarbonate behaves similarly, the hydrochloride melting at 96°, and yielding by treatment with water the corresponding trisubstituted thiocarbamide as a non-basic oil.

Chloroacetyl chloride and bromopropionyl bromide react readily with phenylthiocarbamide, but not to produce additive compounds; instead, two molecules of halogen acid are eliminated, one of which passes off, the other remaining combined with the product, a ring compound, either



"phenylthiohydantoin," PhN:C, or its methylic

homologue, as the case may be.

Acetyl chloride combines with benzyl-*ψ*-thiourea, NH_2·C(NH)·S·CH_2Ph, furnishing the hydrochloride of an acetyl derivative, and, conversely, benzyl chloride unites additively with acetylthiocarbamide; whether the products are identical or isomeric could not be decided owing to the readiness with which they decompose, yielding benzyl mercaptan.

252. "*The Alkyl Compounds of Gold*." By WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON.

The authors have prepared *monoethylauric dibromide*, $(C_2H_5)AuBr_2$, and *amminodiethylauric bromide*, $(C_2H_5)_2AuBr,NH_3$ (compare also *Proc.*, 1907, xxiii., 245).

253. "*The Refractive Power of Diphenylhexatriene and Allied Hydrocarbon*." By IDA SMEDLEY.

The molecular refractions of diphenylbutadiene and diphenylhexatriene (*Proc.*, 1907, xxiii., 162) were measured and compared with those of other hydrocarbons. Sufficient data have been obtained to calculate the influence of the phenyl and the ethenoid groups in unsaturated hydrocarbons. In each case, the refractive power of the group increases markedly as the number of unsaturated groups with which it is conjugated increases. The influence of the hexatriene structure is always greater than that of the benzene ring, a result considered by the author to be at variance with the representation of the benzene molecule as a closely conjugated system of double bonds.

MEETINGS FOR THE WEEK.

TUESDAY, 31st.	Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Astronomy, Old and New," by Sir David Gill, K.C.B., F.R.S., &c.
THURSDAY, Jan. 2nd.	
SATURDAY, „ 4th.	

Royal Institution.—On Saturday next, December 28th, at 3 o'clock, Sir David Gill will deliver the first of the annual course of Juvenile Lectures at the Royal Institution on "Astronomy, Old and New" (illustrated). The remaining lectures will be delivered on December 31st, and January 2nd, 4th, 7th, and 9th.

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